PB81-187288

Assessment of Oil Shale Retort Wastewater Treatment and Control Technology Phases I and II

Monsanto Research Corp.
Dayton, OH

Prepared for

Industrial Environmental Research
Lab.-Cincinnati, OH

Apr 81

U.S. Department of Commerce
National Technical Information Service
NTIS

PB81-187288

EPA 600/7-81-081
April, 1981

ASSESSMENT OF OIL SHALE RETORT WASTEWATER TREATMENT AND CONTROL TECHNOLOGY: PHASES I AND II

by

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Final Report

Contract No. 68-03-2801

March 1981

Project Officer

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-81-081	2. ORD Report	3. RECIPIENT'S ACCESSION NO. PB81 187288

4. TITLE AND SUBTITLE
Assessment of Oil Shale Retort Wastewater Treatment and Control Technology: Phases I and II

5. REPORT DATE
April 1981

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. R. Klieve, G. D. Rawlings, and J. R. Hoeflein

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Monsanto Research Corporation
1515 Nicholas Road
Dayton, OH 45418

10. PROGRAM ELEMENT NO.
CCZN1A

11. CONTRACT/GRANT NO.
68-03-2801

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Protection Agency
Industrial Environmental Research Laboratory-Ci
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
5/79 - 3/80 Final

14. SPONSORING AGENCY CODE
EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Oil shale retorting is a synthetic fuel production technology on the verge of commercialization in the United States. In order to ensure that the emerging oil shale industry will have minimal adverse effects upon surface and/or groundwater where recoverable reserves of oil shale are found, demonstrated technologies to upgrade oil shale wastewaters must be available to developers. To this end, the U.S. Environmental Protection Agency has contracted with Monsanto Research Corporation to conduct a three-year, five-phased study to: 1) summarize known information concerning oil shale retort wastewater sources and characteristics; 2) identify potentially applicable control technologies capable of treating the identified wastewater streams; and 3) design, construct, and operate pilot-plant facilities to evaluate the selected technologies. This report presents results of Phases I and II, in which literature and other information sources were surveyed to obtain relevant data about oil shale retorting technologies, wastewater sources and characteristics, potential wastewater uses, and potentially applicable treatment technologies. As a result of the study, data gaps were identified, and recommendations for bench-scale treatability studies were made.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Oil Shale	Oil	
Wastewater	Waste	
Water Treatment	Water	

18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS *(This Report)* None	21. NO. OF PAGES 99
	20. SECURITY CLASS *(This page)* None	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

New synthetic fuel processes under development must be characterized prior to commercialization so that pollution control needs are identified and control methods can be integrated with process designs. Shale oil recovery processes are expected to have some unique air, water, and solid waste control requirements. This document briefly reviews oil shale retorting technologies, summarizes anticipated characteristics of wastewater streams, discusses concluded and ongoing research activities in the area of retort wastewater treatability, identifies research needs, and recommends a program to fill those needs.

Further information on the environmental aspects of shale oil processing can be obtained from the IERL-Ci Fuels Technology Branch.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

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SECTION 1

INTRODUCTION

Oil shale has been recognized as a potentially substantial energy resource in the United States for more than 100 years. Recently, increasing dependence on foreign oil supplies with rapidly escalating prices has provided new incentive for shale oil recovery from deposits in Colorado, Michigan, Utah, and Wyoming. As a result, a number of domestic companies have completed preliminary process research and development and are now seeking necessary governmental approvals to practice commercial-scale oil shale retorting.

Despite the benefits of oil shale processing as an alternative energy source, its water effluent, air emissions, and solid wastes could have an adverse impact on the environment if discharged untreated. Consequently, pollution control methods capable of adequately controlling environmentally harmful discharges must be available to assure the oil shale industry's compliance with future standards and to avoid potential problems in retrofitting full-scale plants with the necessary technologies. Prior studies by the U.S. Department of Energy, the U.S. Environmental Protection Agency, and industry, have provided some characterization of the environmental effects of this developing technology. However, specific pollution control needs have not been adequately addressed.

The objectives of this 36-month, five-phased study, which began in May 1979, are:

(1) To summarize known information concerning oil shale retort wastewater sources and characteristics;

(2) To identify potentially applicable control technologies capable of treating the identified wastewater streams;

(3) To design operational pilot-plant facilities to evaluate the selected technologies;

(4) To construct the pilot-plant facilities; and

(5) To operate the facilities for one year at three oil shale retorts.

The results of Phases I and II, which were completed as of February 1980 and are presented in this report, consist of:

(1) A survey of pertinent characteristics of oil shale retorting processes and water effluents for use in selecting potentially applicable treatment technologies;

(2) A survey of concluded and ongoing research activities in the area of oil shale retort wastewater treatability; and

(3) Identification of research needs and a recommended research program to meet those needs.

The report concludes with the recommendation that additional bench-scale testing be conducted prior to the selection of an optimum wastewater treatment system and the design of pilot scale testing equipment. Section 3 provides a brief overview of oil shale retorting, summarizes known oil shale wastewater characteristics, and summarizes anticipated water use plans of industry and government contractors outside of industry. Section 4 provides descriptions of known research activities in the area of oil shale wastewater treatability, identifies research needs, and recommends a program to meet those needs. Brief descriptions of oil shale retorting processes and known wastewater characteristics associated with each process are presented in the Appendix.

SECTION 2

SUMMARY

Oil shale retorting is a synthetic fuel production technology on the verge of commercialization in the United States. In order to ensure that the emerging oil shale industry will have minimal adverse effects upon surface and/or ground water where recoverable reserves of oil shale are found, demonstrated technologies to upgrade oil shale wastewaters must be available to developers. To this end, the U.S. Environmental Protection Agency has contracted with Monsanto Research Corporation to conduct a three-year, five-phased study to: 1) summarize known information concerning oil shale retort wastewater sources and characteristics; 2) identify potentially applicable control technologies capable of treating the identified wastewater streams; and 3) design, construct, and operate pilot-plant facilities to evaluate the selected technologies. This report presents results of Phases I and II, in which literature and other information sources were surveyed to obtain relevant data about oil shale retorting technologies, wastewater sources and characteristics, potential wastewater uses, and potentially applicable treatment technologies. As a result of the study, data gaps were identified, and recommendations for bench-scale treatability studies were made.

In-Situ retorting, which consists of heating shale underground after modification of the permeability of the rock formation, is being investigated by Dow Chemical Co., Equity Oil Co., Geokinetics, Inc., Occidental Oil Shale, Inc., and Rio Blanco Oil Shale Co., all of which are now conducting process development efforts. Processes being developed by Paraho Development Corp., Superior Oil Co., TOSCO Corp., and Union Oil Co. are classified as surface retorting, in which mined, crushed shale is heated in aboveground metal vessels to produce crude oil. Although many process variations exist within the two major retorting process categories, *in-situ* and surface, distinct wastewater streams are common to most processes within each category. From *in-situ* retorting, three major streams emanate: mine water, retort water, and gas condensate. Mine water is that water pumped from a shale formation prior to ignition. Retort water is formed when water vapor condenses in cool, rubblized shale ahead of the flame front during retorting. Gas condensate is that water which leaves the retort as a gas and is recovered when gas from the *in-situ* retort is cooled.

From surface retorting, three major streams are envisioned: gas condensate, product water, and spent shale pile leachate. Water normally leaves the surface retort in the vapor phase and is recovered as gas condensate when the retort gas is cooled prior to purification. In addition, water separates from the product oil following oil/gas separation and is termed product water. Since spent shale from surface retorting is expected to be disposed of above ground, leachate through the shale pile is another potential wastewater stream, though the existence of this stream is open to question.

Mine water has been found to exhibit high levels of alkalinity, chemical oxygen demand (COD), chloride, fluoride, sulfate, boron and sodium. Existence of trace metals are of particular concern since some mine water will most likely be discharged to the environment.

Retort wastewater and product wastewater contain high levels of most pollutants identified. Gas condensate wastewaters exhibit high levels of ammonia, alkalinity, and organics; however, concentrations of trace metals are significantly lower in gas condensate than in retort wastewater. Limited data are available to characterize leachate; however, high levels of organics, total dissolved solids (TDS), sulfate and sodium have been exhibited.

Water use schemes developed by industry and government contractors have been reviewed. Most water use schemes suggest use of wastewater within the retorting facility; however, there appears to be little technical information to support this approach. Available information relating to the treatability of individual retort streams were summarized and significant data were only for the treatability of mine water and combined retort/product water.

In the case of mine water, activated alumina absorption, precipitation with phosphoric acid and lime, and ion exchange have been demonstrated in bench-scale screening tests to be able to remove fluoride and/or boron. It is suggested that additional technologies be used for dissolved gas removal, suspended solids removal, TDS removal, and disinfection particularly if the water is discharged or used for potable needs.

Many research studies have focused on the treatment of retort/product water. There remain, however, key technical questions in the area of emulsified oil separation and organics removal. Steam stripping has been identified as a promising technology for dissolved gases removal. Granular activated carbon and polymeric resins have been demonstrated for gross organics removal; however, for cost considerations it is recommended that aerobic biological treatment be focused on for gross organics removal, with carbon and polymeric resins used to remove refractory organics.

No research activity in the area of gas condensate treatment was identified; however, steam stripping should adequately treat gas condensate for in-plant use.

In the case of leachate, it is recommended that funds be used to identify leachate as a major wastewater stream and characterize it, rather than investigate treatment alternatives. If leachate is found to be a significant wastewater stream, serious questions regarding leachate collection arise.

In summary, several technical questions regarding oil shale wastewater treatability exist and should be answered prior to pilot-scale testing. Four sources of mine water, retort water and/or gas condensate for immediate use in bench-scale testing were also identified.

This report was submitted in partial fulfillment of Contract No. 68-03-2801 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1979 to March 1980; work was completed as of February 1980.

SECTION 3

WASTEWATER CHARACTERIZATION

In order to select appropriate strategies for treating wastewater discharges from oil shale retorting operations, the sources of wastewater from these operations must be identified and characterized, and the potential for in-plant reuse must be investigated. To this end, MRC has conducted an industry-wide analysis based on a search of the open literature, industry contacts, and private and government research laboratories. Since no commercial-scale oil shale retort is in operation and no commercial-scale operations are planned before 1982, the resulting industry analysis was based on pilot-plant data, industry plans for full-scale operation, and predictions generated by government contractors outside of industry. Thus, the fact that the oil shale retorting industry is emerging makes the result of the industry analysis no more than a researched prediction.

Presented in this section is a brief discussion of the emerging oil shale industry, expected wastewater sources and characteristics, and a discussion of water use as seen by industry and by national laboratories and government contractors outside of the oil shale industry. A more complete analysis of specific retorting technologies on which discussions in this section are based is presented in Appendix A.

Oil shale retorting technologies can be divided into two categories: surface retorting and *in-situ* retorting (see Figure 1). Surface retorting involves the mining, crushing, and subsequent heating of oil shale in metal vessels aboveground. *In-situ* retorting is a batch operation in which an underground shale formation is heated in place, often modifying the permeability of the rock by fracturing and/or partial mining. If the formation is partially mined before retorting begins, retorting is referred to as modified *in-situ* retorting. In surface retorting, heat to the oil shale can be transferred by either a gas or solid medium. In addition, combustion for heat production can be generated within the surface retort or outside of the retort.

Several different sources of wastewater are associated with each individual retorting technology, and there are several types of wastewater characteristics for both major retorting types, surface and *in-situ*. In the case of surface retorting, water normally leaves the retort in the vapor phase and is recovered

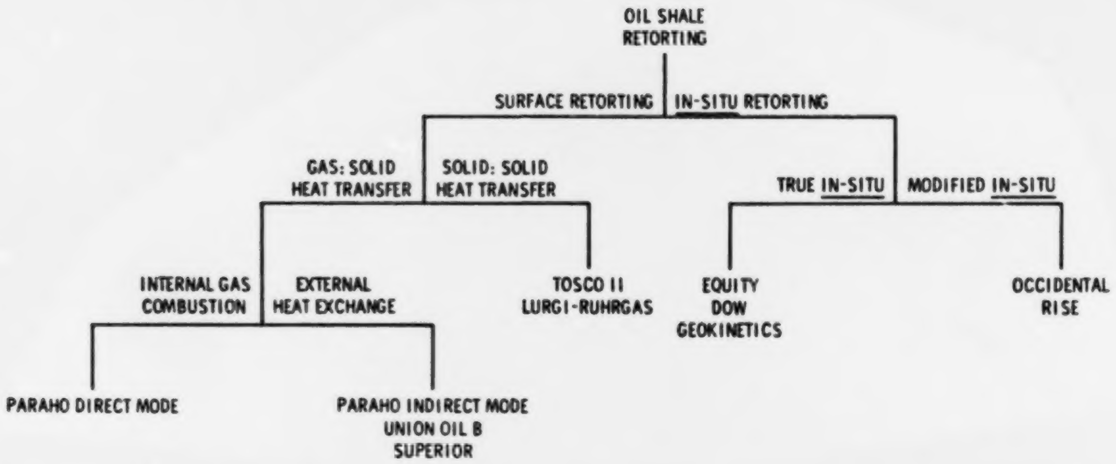
OIL SHALE RETORTING
SURFACE RETORTING
IN-SITU RETORTING
GAS: SOLID HEAT TRANSFER
SOLID: SOLID HEAT TRANSFER
TRUE IN-SITU
MODIFIED IN-SITU
INTERNAL GAS COMBUSTION
EXTERNAL HEAT EXCHANGE
TOSCO II
LURGI-RUHRGAS
EQUITY
DOW
GEOKINETICS
OCCIDENTAL
RISE
PARAHO DIRECT MODE
PARAHO INDIRECT MODE
UNION OIL B
SUPERIOR

Figure 1. Classification of retorting process.

as gas condensate when the retort gas is cooled prior to purification. In addition, some water separates from the product oil following oil/gas separation. Since spent shale from surface retorting is expected to be disposed of above ground, leachate from the spent shale piles may be another wastewater stream unique to surface retorting of shale oil. Thus, the major categories of wastewaters expected from surface retorting are:

- Gas condensate
- Water separated from the product oil (product water)
- Retort water (Union Oil B process only)
- Leachate

If water is encountered during shale excavation for surface retoring, a mine water waste stream can also be expected.

In the case of *in-situ* retorting, water vapor produced in the retorting zone normally condenses in the oil shale ahead of the retorting zone, and continues to move through the unretorted rubblized shale as a liquid. This water is recovered as a liquid with the product oil and is normally termed retort condensate or retort water. As with surface retorting, some water remains as a vapor and is recovered as gas condensate when the gas recovered from the *in-situ* retort is cooled. Since *in-situ* retorts must be dewatered prior to igniting, *in-situ* retorting results in an additional wastewater stream--mine water. Thus, three major categories of wastewaters are expected from *in-situ* retorting:

- Retort water
- Mine water
- Gas condensate.

In order to characterize expected oil shale retorting wastewaters to the degree necessary to select potential treatment technologies, MRC has gathered analytical data, where it exists, for each wastewater stream from each oil shale retorting technology. As has been noted by other investigators [1] who have analyzed oil shale wastewaters, interferences often occur when state-of-the-art techniques are used to analyze certain constituents, e.g., chlorides and sulfates, in oil shale wastewaters. Most of the data listed in Appendix A were obtained via state-of-the-art techniques and these data should be carefully interpreted in accordance with the analytical method used. The data does serve, however, to identify major groups of pollutants associated with each oil shale wastewater and errors in the absolute concentration of the pollutants; that is, gross pollutants can be identified, but the absolute concentration may be inaccurate by an order of magnitude. Based on the literature search, maximum observed concentrations of major constitutents in each retort wastewater stream are listed in Table 1. The mine water characterization data listed in Table 1 is based on data gathered at the retort sites of four developers: Occidental, Geokinetics, Rio Blanco, and Equity. For most pollutant categories, data obtained at Geokinetics' Kamp Kerogen site provided the highest observed concentrations. As can be seen in Table 1, mine water can potentially exhibit high levels of alkalinity, COD, chloride, fluoride, sulfate, boron and sodium, which are of primary concern because, unlike other retorting wastewaters, some mine water will most likely be discharged in some degree to the environment.

Retort water, or water which has condensed in an *in-situ* retort, will most likely be the most difficult wastewater to treat and will probably not be directly discharged to the environment. As can be seen in Table 1, retort water contains high levels of most pollutants identified. Again, recent data obtained by MRC at Geokinetics' Kamp Kerogen site accounts for the highest observed pollutant levels in most categories.

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[1] Fox, J. P., D. S. Farrier, and R. E. Poulson. Chemical Characterization and Analytical Considerations for an *In-Situ* Oil Shale Process Water. Report LETC/R1/78/7. Laramie Energy Technology Center. U.S. Department of Energy, November 1978.

TABLE 1. MAXIMUM OBSERVED CONCENTRATION OF MAJOR CONSTITUENTS IN OIL SHALE WASTEWATER STREAMS

mg/L[a,k]

	Mine water[b,c]	Retort water[c,d]	Gas condensate[e,f]	Leachate[g,h]	Product water[h,i]
Alkalinity (as $CaCO_3$)	25,200	17,800	68,550	ND[j]	35,200
pH	7.7-9.3	8.4-8.9	8.5-9.8	4.3-11.1	7.6-8.6
BOD	ND	2,000	14,075	ND	75,000
COD	6,090	17,500	26,550	ND	75,700
TOC	11	2,150	29,200	400	32,800
TKN	5.8	4,880	31,400	ND	33,600
TSS	1,970	84	200	ND	137,000
TDS	37,600	9,690	7,470	37,000	160,000
Oil and grease	3	186	502	ND	964
Phenols	<1	38	260	47	19
HCO_3^-	26,000	17,200	31,265	29.4	1,500
CO_3^-	2,380	9,780	30,500	ND	28,900
Cl^-	2,200	3,000	1,100	3,080	7,000
CN^-	<1	95	33	ND	5.2
Fl^-	93	35	<1	20	2
NO_3^-	6.2	9,500	288	<1	2,570
NO_2^-	<1	1.3	<1	ND	<1
Phosphate	5	4.3	4.2	ND	33
Sulfate	11,100	1,827	930	90,000	9,140
Sulfite	ND	400	390	ND	5
Sulfide	17	447	1,012	ND	ND
Sulfur	ND	1,230	1,540	ND	43,200
NH_3	25	5,667	17,000	ND	32,500
NH_4^+	ND	6,200	17,000	ND	4,080
Al	<1	<1	<1	<1	4.6
As	<1	2.6	<2	<1	9
Ba	<1	2.0	<1	<1	2
B	88	61	<20	3	35
Ca	95	32	60.7	3,150	76
Cu	<1	1.9	<1	<1	9
Fe	13	14	>10	<1	7
Pb	<1	<1	<1	<1	2.25
Li	<1	1.5	<10	ND	1
Mg	43	32	25	4,720	540
Hg	<1	<1	<7	ND	13.5
Mo	<1	11.9	<1	10	1.9
Ni	<1	1.62	<1	<1	<2
K	54	121	<5	1,460	35
Se	<1	<1	1	<1	12.5
Si	13	8	9	47	32
Na	10,455	9,392	35.5	35,200	290
Sr	<1	<1	<1	14	3
Zn	<1	6.9	<1	1.1	1.2
Cl_2	<1	ND	<1	ND	2.0
Fl_2	ND	ND	<1	ND	7.0
P	ND	ND	ND	ND	5.0
Hardness	417	286	152	ND	ND

[a] Except pH given in pH units.

[b] Ag, Be, Bi, Br, Cd, Co, Cr, Ge, Mn, Se, and V were also analyzed in one or more samples, however, none were found in concentrations >1 mg/L.

[c] Primary wastewater stream in *in-situ* retorting.

[d] Ag, Be, Bi, Br, Cd, Co, Cr, Cs, Ge, Mn, Ti, Tl, Sn, and V were also analyzed in one or more samples, however, none were found in concentrations >1 mg/L.

[e] Ag, Cd, Co, Cr, Cs, Ga, La, Mn, Pr, Rb, Sc, Sn, Ti, U, V, Y, and Zr were analyzed in one or more samples, however, none were found in concentrations >1 mg/L.

[f] Wastewater stream common to both surface and *in-situ* retorting.

[g] Ag, Be, Cr, Mn, and V were also analyzed in one or more samples, however, none were found in concentrations >1 mg/L.

[h] Primary wastewater stream in surface retorting.

[i] Ag, Cd, Co, Cr, Cs, Ga, Ge, Mn, Sb, Sc, Sn, Ti, and V were also analyzed in one or more samples, however, none were found in concentrations >1 mg/L.

[j] No data.

[k] Note that reported concentrations are not representative of anticipated commercial scale retorting streams.

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Gas condensate is a wastewater stream which will emanate from both *in-situ* and surface retorting; however, data presented in Table 1 are largely based on analysis of gas condensate from two surface retorting technologies: Paraho and Tosco. As with retort water, gas condensate exhibits high levels of organics, bicarbonate, and ammonia; however, concentrations of dissolved trace metals and other inorganics are significantly lower in gas condensate than in retort water.

Investigators in oil shale wastewater research are undecided as to whether leachate from spent shale piles characteristics of surface retorting will be a major wastewater stream. Since leachate may potentially be a major wastewater stream from *in-situ* retorting, it has been considered in Table 1, and will be addressed when control technologies are discussed. As seen in Table 1, no data is available to predict concentrations of many pollutants, particularly organics, nitrogen compounds, and sulfur compounds. Based on available data, high levels of TOC, TDS, sulfate, and sodium can be expected in spent shale pile leachates.

Product water, or water which separates from product oil, will be difficult to treat. Organics, probably originating from oil emulsions, are more prominent in product water than in retort water.

In reviewing industry development plans, and in conversations with several oil shale developers, it is quite apparent that many developers do not have firm plans for either reusing or discharging oil shale wastewaters. Even more undefined at this time are the wastewater treatment systems which will be used to upgrade a wastewater for a particular reuse application or for discharge. General statements regarding no planned discharge have been made; however, there appears to be no information in the literature to support this approach. For example, the development plans of some surface retorting developers indicate use of all retort waters for spent shale moisturization and compaction. This may or may not be feasible, as some data indicates that retort water produced may be nearly three times the volume of that needed for standard shale moisturization to 14% weight.

Some water reuse diagrams have been suggested by government contractors outside of industry, particularly for the Paraho direct heated process, the Tosco II process, the Occidental process, and the RISE/Lurgi-Ruhrgas process. These diagrams provide closed loop (complete recycle) water reuse schemes, though many assumptions regarding wastewater treatment technology performance and water quality needs are made. These diagrams, as well as available information from developers concerning water use schemes can be found in Appendix A.

Indecisiveness on the part of industry to commit themselves to a particular water reuse scheme and particular wastewater treatment technologies is the result of several deficiencies in the oil shale wastewater data base. These include:

- Lack of data in the areas of wastewater characterization and wastewater flow rates. In part, this deficiency derives from the fact that much of this data can only be obtained from full-scale operations, which do not exist;
- Lack of data in the area of water quality needs for various retorting process components; and
- Lack of data in the area of wastewater treatability.

As data is provided, in part by government research activities, industry will begin to make commitments to water use schemes based on economic considerations.

For the purposes of this contract (providing wastewater treatability data for oil shale wastewaters), MRC has summarized industry and government contractor water use ideas into four diagrams shown in Figures 2 through 5. These diagrams provide a frame work of treatment steps which must be provided before a particular wastewater can be used for one of many potential applications. Once specific technologies are pilot-tested, economic data on which water reuse decisions can be based will be provided.

Mine water from dewatering of the *in-situ* retort prior to ignition could be an important water resource in the water-short Colorado River basin. Therefore, cooling tower makeup, boiler feed water, and drinking water are included as potential uses of mine water as shown in Figure 2. Due to potentially unsatisfactory concentrations of H_2S, volatile organics, Fl^-, B, and TDS, mine water will have to be treated prior to discharge for removal of these species.

Extensive treatment will be necessary if retort water and product water are to be discharged, as shown in Figure 3. More realistically, these wastewaters will be treated to the degree necessary for use in a thermal sludge oxidizer, for dust control for spent shale moistening from a surface retort associated with a modified *in-situ* retort and/or for cooling water makeup.

Similarly, there are several realistic uses for gas condensate at the retorting site as shown in Figure 4.

As mentioned, leachate may or may not be a primary wastewater stream. Based on current analytical data, it appears TDS and trace metal removal will be necessary before leachate can be discharged to surface waters; however, there are several potential in-plant uses for leachate requiring a lesser degree of treatment as shown in Figure 5.

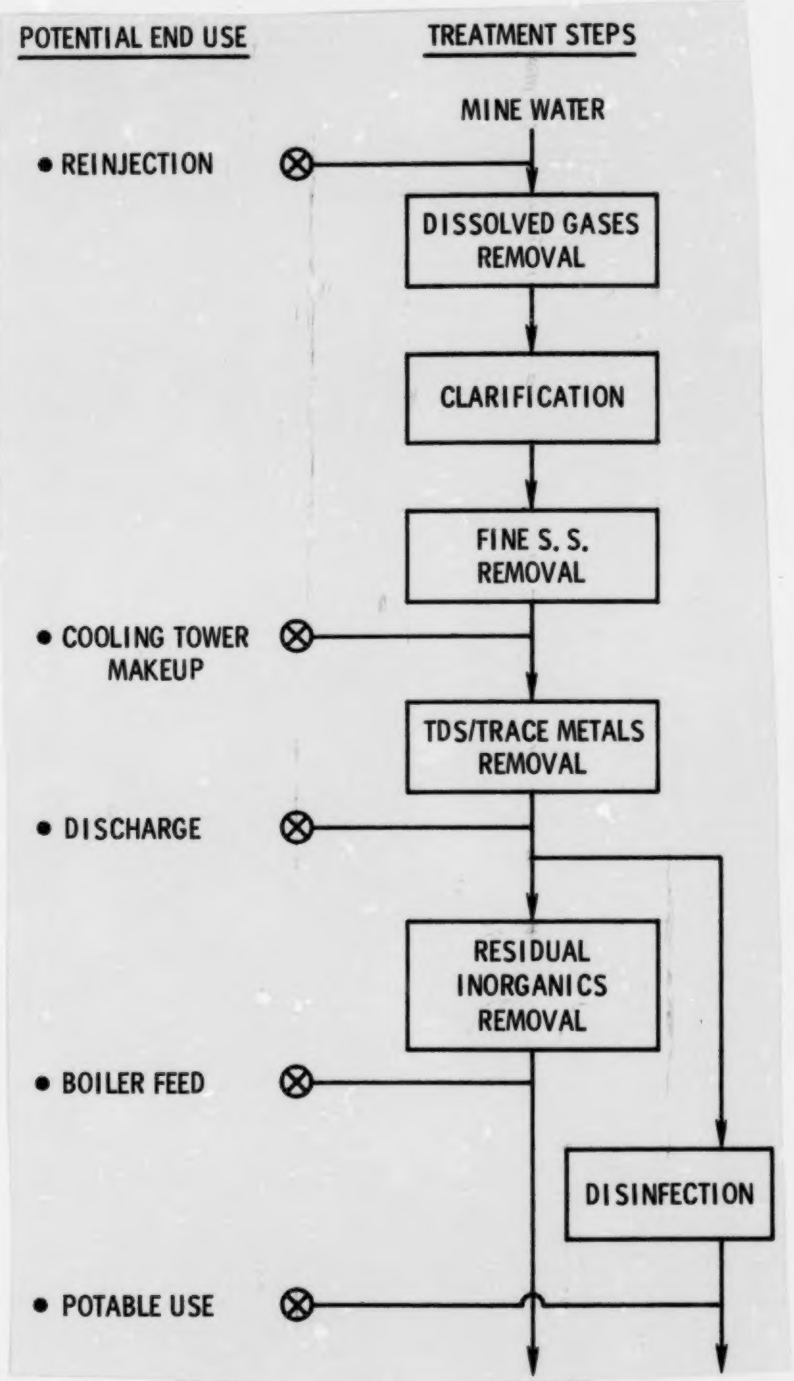
POTENTIAL END USE
TREATMENT STEPS
MINE WATER
• REINJECTION
DISSOLVED GASES REMOVAL
CLARIFICATION
FINE S. S. REMOVAL
• COOLING TOWER MAKEUP
TDS/TRACE METALS REMOVAL
• DISCHARGE
RESIDUAL INORGANICS REMOVAL
• BOILER FEED
DISINFECTION
• POTABLE USE

Figure 2. Mine water treatment steps and reuse potential.

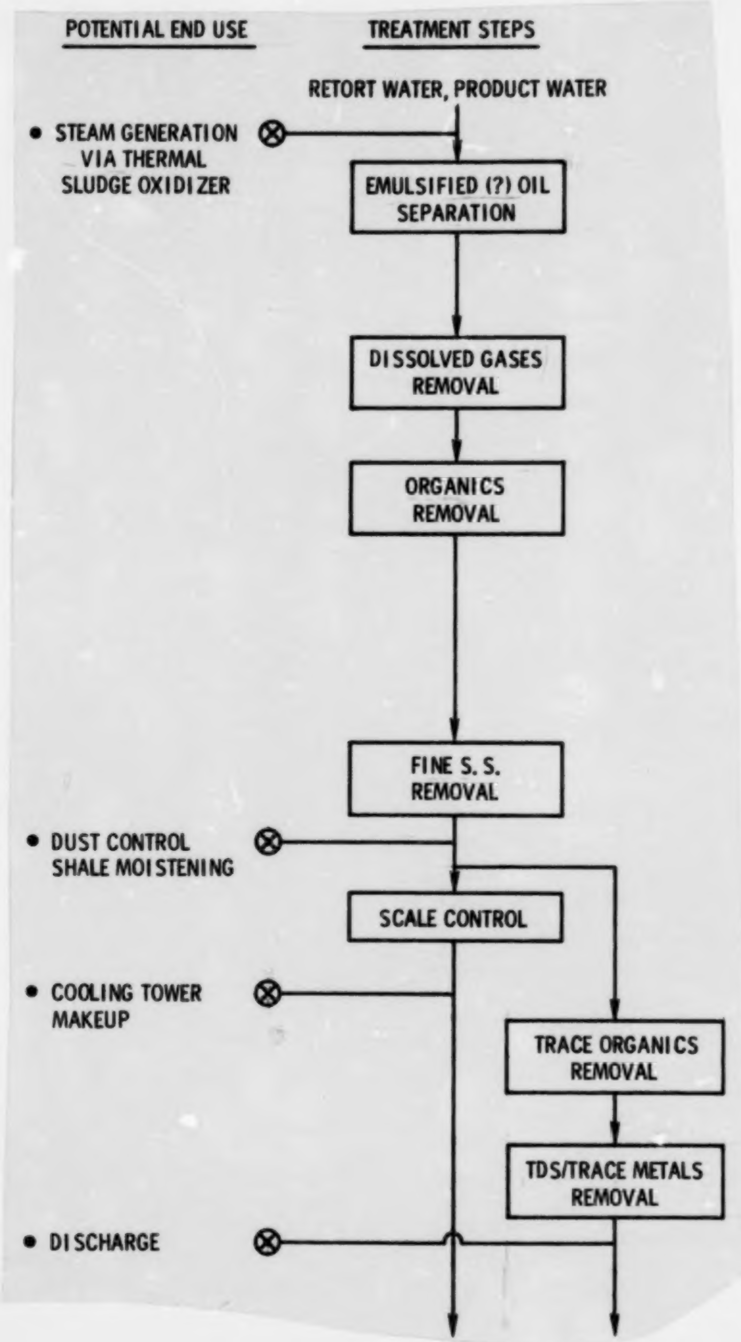
POTENTIAL END USE
TREATMENT STEPS
RETORT WATER, PRODUCT WATER
• STEAM GENERATION VIA THERMAL SLUDGE OXIDIZER
EMULSIFIED (?) OIL SEPARATION
DISSOLVED GASES REMOVAL
ORGANICS REMOVAL
FINE S. S. REMOVAL
• DUST CONTROL SHALE MOISTENING
SCALE CONTROL
• COOLING TOWER MAKEUP
TRACE ORGANICS REMOVAL
TDS/TRACE METALS REMOVAL
• DISCHARGE

Figure 3. Retort wastewater treatment steps and reuse potential.

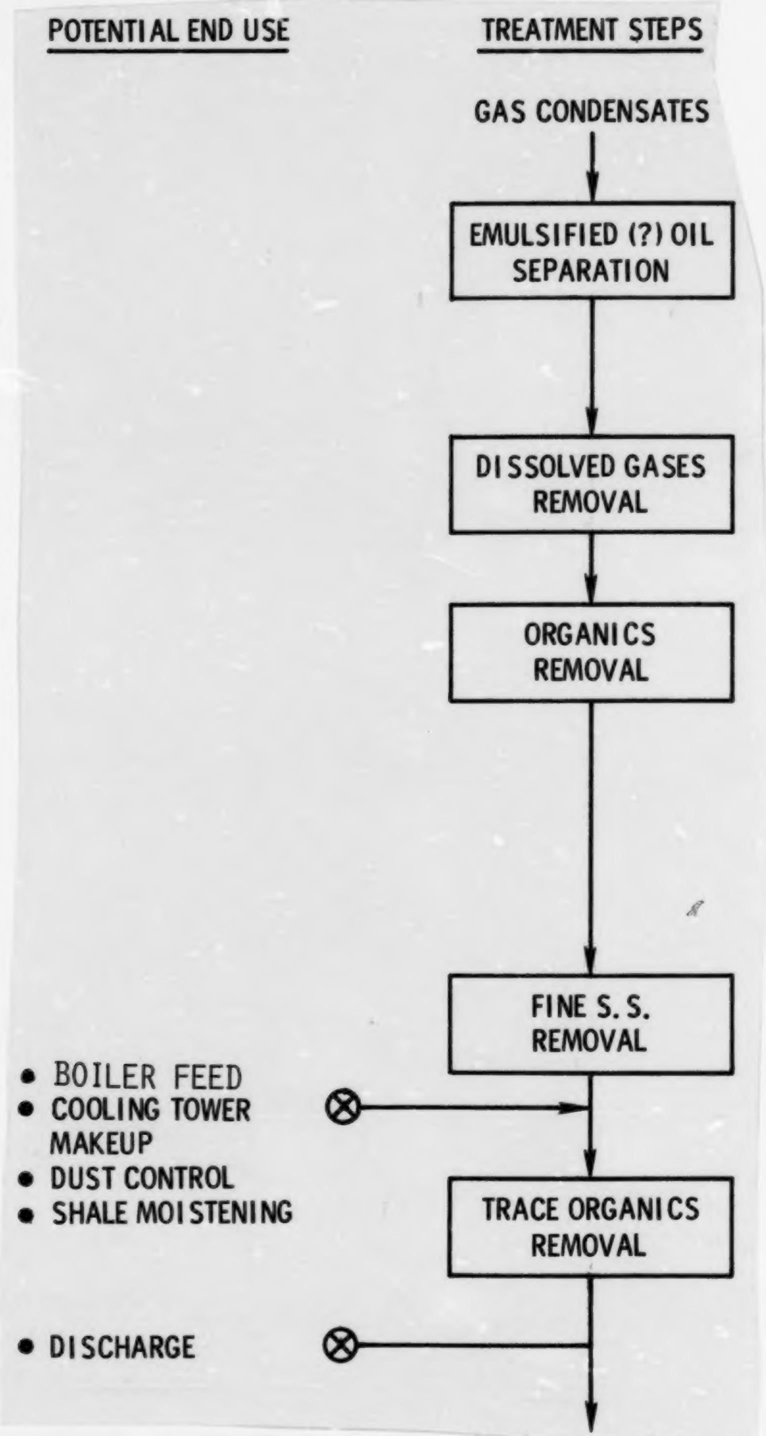
POTENTIAL END USE
TREATMENT STEPS
GAS CONDENSATES
EMULSIFIED (?) OIL SEPARATION
DISSOLVED GASES REMOVAL
ORGANICS REMOVAL
FINE S. S. REMOVAL
• BOILER FEED
• COOLING TOWER MAKEUP
• DUST CONTROL
• SHALE MOISTENING
TRACE ORGANICS REMOVAL
• DISCHARGE

Figure 4. Gas condensate wastewater treatment steps and reuse potential.

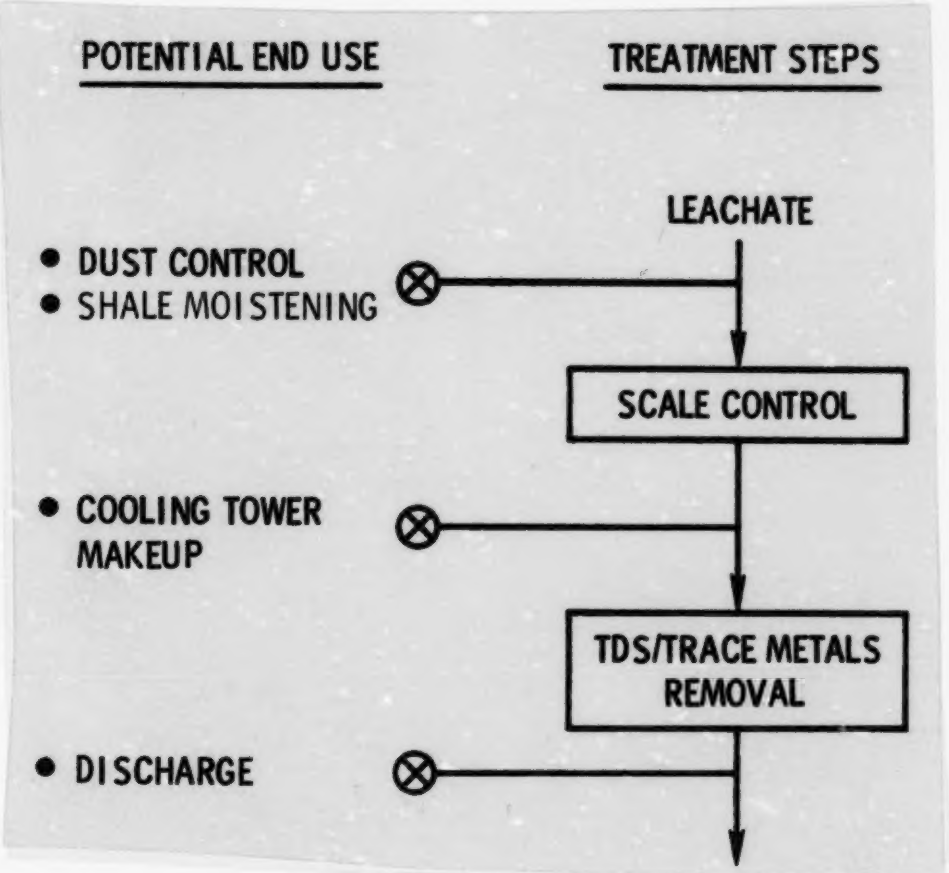
POTENTIAL END USE
TREATMENT STEPS
LEACHATE
• DUST CONTROL
• SHALE MOISTENING
SCALE CONTROL
• COOLING TOWER MAKEUP
TDS/TRACE METALS REMOVAL
• DISCHARGE

Figure 5. Leachate treatment steps and reuse potential.

SECTION 4

TREATMENT OF OIL SHALE WASTEWATERS

INTRODUCTION

In an effort to identify potential technologies for use in pilot-scale oil shale wastewater treatment systems, MRC conducted a second literature search to identify bench-scale research work dealing with the treatability of oil shale wastewaters. It was hoped that an adequate data base would exist for identification of potential technologies which could be pilot-tested; however, it is now apparent that the existing data base is limited. Of the four wastewaters identified in Section 3, treatability data exists for mine water and retort water, though, as will be seen in this section, the results of these studies are largely inconclusive since the studies were preliminary. It was also found that several key studies on the treatability of retort water are either now ongoing, or have been completed though a published report not yet available. This section, therefore, presents summaries of concluded and published research studies as they relate to the four wastewater streams identified in Section 3: mine water, retort wastewater, gas condensate, and leachate. Where published data do not exist for a particular study, a summary based on project status report or personal communications will be presented. Following the subsections covering the treatability of individual wastewater streams, a discussion leading to recommendations for further study will be presented.

MINE WATER

As discussed in Section 3, water pumped from *in-situ* retorts prior to ignition may contain unacceptable levels of fluoride, phenols, boron, and TDS if the water is to be discharged or used for potable purposes.

Treatability studies have been conducted by Battelle N.W. [2] to evaluate methods for removing fluoride and boron from minewater.

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[2] Mercer, B. W., W. Wakamiya, R. R. Spencer and M. J. Mason. Assessment of Control Technology for Shale Oil Wastewaters. Paper presented at DOE Environmental Control Technology Symposium, November 1978.

The results of bench-scale experiments with groundwater taken from a site in Colorado show a 50% breakthrough capacity of 350 bed volumes for fluoride removal by activated alumina adsorption. The groundwater fluoride concentration was 20 mg/L; therefore, the fluoride capacity was approximately 7 g/L of activated alumina. In order to achieve effective fluoride removal, the feed was adjusted to pH 2.5 for the initial 100 bed volumes to reduce the effluent pH to about 9. Thereafter, the feed pH was adjusted to pH 5.5, which is the optimum level for fluoride removal. Since the alumina bed was regenerated with dilute sodium hydroxide, it was necessary to add additional acid to the feed at the beginning of the exhaustion cycle to neutralize the residual caustic regenerant in the bed. The acid addition for pH adjustment of the feed is expected to represent a substantial portion of the chemical cost of treatment for fluoride removal by activated alumina adsorption. Battelle N.W. estimated that 13¢ per thousand gallons of groundwater would be required to adjust the pH with sulfuric acid priced at $50 per ton of acid. Regenerant costs were estimated to be 16¢ per thousand gallons of groundwater treated based on sodium hydroxide priced at $280 per ton.

Results of Battelle's precipitation experiments with simulated groundwater indicate 90% fluoride removal with phosphoric acid and lime addition. Approximately 9 moles of phosphorus and 10 moles of calcium per mole of fluoride were required to achieve a level of fluoride removal needed to allow discharge to nearby surface receiving waters. The precipitation formed was basically a mixture of fluorapatite, $Ca_5F(PO_4)$, and hydroxy apatite, $Ca_5(OH)(PO_4)_3$. The cost of phosphoric acid and lime to treat the groundwater was estimated by Battelle to be about $2 per thousand gallons, which was found to be excessive, relative to other treatment methods.

Ion exchange with a weak base anion exchange resin was also investigated by Battelle as a unique process which showed some potential because of the low selectivity of this resin for bicarbonate, the principal ion competing with the fluoride. Laboratory results showed a correspondingly low selectivity for fluoride which negates possible advantages this process may have over other ion exchange processes.

Battelle also found that boron removal from the groundwater was not effected by either activated alumina or lime and phosphate treatment. Bench-scale studies with a boron selective ion exchange resin indicated good boron removal from 2,000 bed volumes of groundwater containing 0.6 mg/L. Boron removal to less than 0.3 mg/L is required for discharge.

Reverse osmosis or electrodialysis are discussed by WPA [3] as candidate processes which may be commercially viable in treating mine drainage waters. It was pointed out that electrodialysis will only separate those molecules which are in ionic form in solution. Boron, for example, requires that the solution pH be about 8.5 to 9 to become ionic. In general, electrodialysis also does not have a capability for separating soluble organic molecules which may exist in minewater. Reverse osmosis, on the other hand, has a moderate capability for separating boron from acidic waters, and it is only at a quite high pH (~N 9.5-10) that a 75% rejection of boron is attained. Phenol rejection is significant only at high pH as well and fluoride rejection is typically about 90%. Both reverse osmosis and electrodialysis require a moderate to good level of prefiltration to remove suspended solids which will be contained in the mine water. Since mine water is alkaline, electrodialysis would require pretreatment with sulfuric acid to prevent scaling on the membranes. Acid addition or chelating agents may also be required to prevent precipitation of salts, if the reverse osmosis is used. WPA emphasizes that both reverse osmosis and electrodialysis would provide a product with a lower total dissolved solids than required for discharge. As a rule, reverse osmosis would give the lowest TDS product with a typical value for the mine water considered of from 100 to 200 mg/L, while the electrodialysis product might range from 200 to 400 mg/L.

WPA previously made study cost estimates for both membrane processes without disposal of the concentrated solutions and without boron and phenol removal. The costs for the two processes are similar, although electrodialysis would become less attractive at the higher end of the TDS range. Reverse osmosis costs are not significantly dependent on influent TDS and have the added advantage that the system can be operated to remove boron, phenol, and ammonia.

Concentrate streams will be generated by both reverse osmosis and electrodialysis. If it is assumed that an 85% recovery and 90% separation of the dissolved solids is attained, then the concentrate stream would have about 6 times the concentration of the mine water and about one-seventh its volume. WPA points out that the cost of disposal of this stream, ranging from about 0.3 to 2.0 million gallons per day, could be a major part of the treatment cost. Concentrate disposal could be either by evaporation in ponds or preferably in a vapor compression (RCC) evaporator. If a "thermal sludge" or similar type unit is used on site for steam raising, it may prove possible to blend the concentrate with the feed to this unit. The concentrate would contain sodium bicarbonate, possibly near its solubility limit and it may prove possible to recover this material for sale, particularly as both CO_2 and excess heat are readily available at an oil shale plant.

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[3] Water Purification Associates Quarterly Status Report, May 1, 1979 - August 31, 1979. A Study of Aerobic Oxidation and Allied Treatments for Upgrading *In-Situ* Retort Waters. Submitted to U.S. Department of Energy, Laramie Energy Technology Center.

Removal of dissolved gases (H_2S, CH_4, CO_2) and oxidation and removal of dissolved iron from mine water may be necessary before reverse osmosis, electrodialysis, or ion exchange can be used to remove boron and fluoride. Simple aeration has been quite successful for these purposes [4]. Gravity aerators such as cascades or stacks of perforated pans or troughs are commonly used in water purification plants. Other forms of aerators are spray aerators, diffusers, and mechanical aerators.

RETORT WATER

Of the wastewater streams identified in Section 3, retort water treatability has drawn the most attention from researchers because of its unique and complex character. As can be seen in Table 2, many attempts have been made or are being made with a variety of techniques to treat retort water. Some studies have been completed resulting in published, public reports (indicated by "A"); however, the results of many studies are unavailable to the public (indicated by "B", "C", or "D") for various reasons.

In one series of studies, Harding and Associates at the University of Colorado conducted "preliminary bench-scale treatment evaluations" of activated carbon adsorption, polymeric adsorption, thermal stripping, and weak acid ion exchange [5, 6]. They have also conducted evaluations of the wet air oxidation process, though results have not yet been published (personal communication, E. R. Bennett, University of Colorado, to G. D. Rawlings, Monsanto Research Corporation, November 8, 1979).

In studies of activated carbon adsorption, raw retort water was passed through six columns in series filled with an unspecified activated carbon at a flow rate of about 1 BV/hr. Over a 17 hr period, COD removals better than 75% were consistently observed (influent COD = 12,500 mg/L). In addition, phenol removal was 100% (influent phenol = 31 mg/L) during a single observation after 2 hr of operation. The investigators noted fouling of the carbon surface was occurring since breakthrough curves for COD removal showed no sharp inflection, and head losses through the column developed rapidly. They suggest that pretreatment for removal of oil and suspended material may yield better performance of activated carbon adsorption.

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[4] Fair, G. H., J. C. Geyer, and D. A. Okun. Water and Wastewater Engineering: Volume 2. John Wiley & Sons, Inc., 1968.

TABLE 2. STATUS OF RESEARCH STUDIES FOCUSING ON THE TREATABILITY OF RETORT WATER

Unit process	University of Colorado	University of California at Berkeley/ Lawrence Berkeley Laboratory	Amoco	Battelle Pacific Northwest Laboratories	Water Purification Associates	University of Southern California	Laramie Energy Research Center	Resources Conservation Company	Osmonics, Inc.
Chemical precipitation		D[a] [7]		C[b] [12, 13]			A[c] [15]		
Ion exchange	A [5, 6]		B[d] [11]				A [15]		
Adsorption on activated carbon	A [5]			A [2]	D [3]		A [15]		
Adsorption on polymeric resins	A [5]				D [3]				
Adsorption on spent shale		A [8, 9]	B [11]						
Anaerobic fermentation		A [10]		A [2]					
Aerobic biological treatment		D [7]	B [11]	A [2]	C [3]	A [14]			
Stripping (air or steam)	A [5]		B [11]	A [2]	C [3]				
Solvent extraction			B [11]	C [12]	D [3]				
Ozonation			B [11]			A [14]			
Evaporation								D[f]	
Wet air oxidation	C[e]								
Electrolytic						A [14]			
Photodegradation						A [14]			
Permanganate addition						A [14]			
Reverse osmosis					D [3]				A [16]
Physical oil/water separation							D[g]		

[a] D - laboratory work planned or in progress.

[b] C - laboratory work completed; report to be prepared.

[c] A - laboratory work completed; report available to public.

[d] B - laboratory work completed; report unavailable to public.

[e] Conversation with E. R. Bennett, University of Colorado, November 8, 1979.

[f] Conversation with W. Wakamiya, Battelle, N.W., November 12, 1979.

[g] Conversation with Trudy Phillips, Laramie Energy Research Center, November 27, 1979.

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[5] Harding, B., K. D. Linstedt, E. R. Bennet, and R. E. Paulson. Study Evaluates Treatments for Oil-Shale Retort Water. Industrial Wastes, September/October 1978.

[6] Harding, B. L., K. D. Linstedt, E. R. Bennett, and R. E. Paulson. Removal of Ammonia and Alkalinity from Oil Shale Retort Waters by the Use of Weak Acid Cation Exchange Resins. Proceedings of the Second Pacific Chemical Engineering Congress, 1977.

[7] Fox, P. Spent Shale as a Control Technology for Oil Shale. October Monthly Progress Report submitted to Charles Grua. U.S. Department of Energy, November 1979.

[8] Fox, J. P., R. N. Cenaclerio, D. E. Jackson and S. L. Lubic. Spent Shale as a Control Technology for Oil Shale Retort Water. Quarterly Progress Report June 1, 1978 - September 30, 1978 submitted to U.S. Department of Energy, January 1979.

[9] Jackson, D. E. and J. P. Fox. Spent Shale as a Control Technology for Oil Shale Retort Water. Quarterly Progress Report - October 1, 1978 - December 31, 1978 submitted to U.S. Department of Energy, January 1979.

[10] Oggio, E. A., J. P. Fox, J. F. Thomas and R. E. Paulson. Anaerobic Fermentation of Simulated In-Situ Oil Shale Retort Water. Presented at te Meeting of the American Chemical Society, March 1978.

[11] Internal Amoco Report, June 1979.

[12] Mercer, B. W. Analysis, Screening and Evaluation of Control Technology for Wastewater Generated in Shale Oil Development. Quarterly Report October - December 1978.

[13] Mercer, B. W. Analysis, Screening and Evaluation of Control Technology for Wastewater Generated in Shale Oil Development. Quarterly Report July - September 1978.

[14] Yen, T. F., et al. Degradation of the Organic Compounds in Retort Water. Final report submitted to R. E. Paulson, Laramie Energy Research Center, U.S. Department of Energy.

[15] Hubbard, A. B. Method for Reclaiming Wastewater from Oil Shale Processing. U.S. Department of the Interior, Bureau of Mines, and Laramie Energy Research Center.

[16] Osmonics, Inc. Application Test Report for Laramie Energy Research Center July 10, 1979.

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Harding also investigated the use of synthetic polymeric adsorbents. Four Rohm & Haas resins (XAD-2, XAD-4, XAD-7, and XAD-8) were screened in preliminary column tests, while only XAD-4 which demonstrated the best performance in the screening study was evaluated in longer-term tests. In the XAD-4 test, 20 BV of filtered retort water was applied at a rate of 6 BV/hr. Initially, COD removal was 84% (initial COD = 12,400 mg/L); however, performance worsened with time, so that only 24% of the COD was removed at the end of the test. The authors stated that low polarity resins out performed higher polarity resins in the removal of COD. They suggest that coupling polar and nonpolar resins may yield an effluent with more acceptable COD levels.

Harding also investigated thermal stripping to remove ammonia, alkalinity, and COD from the retort water. Retort water at 60°C was introduced to the top of a 1010 cm x 5 cm packed column at a rate of 250 mL/min and recirculated through the column 3 times. Air was passed countercurrently at a rate of 90 L/min. NH_3 and CO_2 were removed simultaneously; however, COD was not removed. The authors caution against developing any rate constants from the study, since the experimental apparatus was small, the column was not insulated, and the temperature of the waste dropped 20°C after passing through the column. The study is significant though, in that it indicates simultaneous NH_3 and CO_2 removal without pH adjustment.

Weak acid ion exchange was also examined for simultaneous NH_3 and CO_2 removal. First, Duolite CC-3 was placed in a column, and retort water was introduced to the column in an upflow mode. The column immediately filled with CO_2, however, excellent NH_3 removals were observed. The investigators then conducted a series of batch tests which demonstrated excellent simultaneous removals of NH_3 and CO_2. Fouling of the resins by organics, and evaluation of CO_2 were identified as problems with ion exchange.

As mentioned, studies investigating wet air oxidation of retort water were also conducted at the University of Colorado, though, published results are not available. The investigators have indicated that excellent removals of COD were observed. The studies were conducted at 1,500 psig, using pure oxygen, with temperatures ranging from 100°C to 325°C. In one run, COD was reduced from 10,000 mg/L to 200 mg/L. The concentration of ammonia stayed about the same.

Fox and Associates have investigated spent shale adsorption as a means to remove both inorganic and organic carbon from retort studies [8, 9]. In batch and column tests, excellent removals of inorganic carbon were demonstrated (up to 98%); however, organic removal was not as significant. The investigators suggest that spent shale adsorption of inorganic carbon and NH_3

removal by stripping be used as an alternative to chemical pH adjustment prior to CO_2 and NH_3 stripping in a retort wastewater treatment system.

Fox has also investigated anaerobic fermentation of retort water [10]. Based on four experiments, the investigators offer the following conclusions:

1. The retort water studied had to be pretreated to remove toxic and add deficient constituents before it could be successfully treated with the anaerobic fermentation process. Pretreatment included pH adjustment to 7, ammonia reduction and nutrient addition.
2. A digested sludge from a conventional municipal sewage treatment plant was successfully acclimated to the retort water studied.
3. A major fraction of the organics in the retort water studied was stabilized by conversion to CH_4 and CO_2 using the anaerobic fermentation process. BOD_5 and COD removal efficiencies were 76% to 80%. Within the limits of experimental error, the same removal rate was obtained for both BOD_5 and COD.
4. The effluent from anaerobic fermentation of the retort water studied (BOD_5: 530 mg/L to 580 mg/L) may be suitable for treatment by conventional aerobic processes.
5. The growth of the methane formers, which stabilize the organics, was nutrient limited in the retort water studied.
6. The pretreatment of the retort water studied removed 49% of the BOD_5. This was probably due to the reduction in solubility of high molecular weight fatty acids at neutral pHs; they drop out of solution and do not exert a BOD.
7. A major component removed from the retort water studied during anaerobic fermentation was fatty acids.
8. The long hydraulic residence time used in this study (50 days) would not be used in practice. Cell recycle, which increases the cell residence and decreases the hydraulic residence time, would be exploited to achieve hydraulic residence times on the order of 2 to 3 days.

In-house screening studies have been conducted by Amoco utilizing Geokinetics' retort water which had been pretreated with alum coagulation and sand filtration [11]. Tests with weak acid cationic exchange resins, similar to those conducted by Harding were conducted and resulted in similar findings. As in the

Harding tests, Amoco found that ion exchange holds some potential for NH_3 removal; however, CO_2 evaluation would be a problem in a column operation.

Amoco also investigated spent shale absorption as a means to remove organic carbon from retort water. In batch and column tests utilizing Lurgi spent shale, little or no organic carbon removal was observed.

Several tests were conducted utilizing aerobic biological treatment with limited success. Batch reactors were used to treat three dilutions (60:1, 40:1, 20:1) of both raw retort water and retort water which had been steam stripped. Over a 20-day period, TOC reduction never exceeded 50%, indicating a high level of refractory organics. Removal of NH_3 in the reactors only occurred with the 40:1 and 60:1 dilutions.

Amoco observed 95% removals of ammonia and carbonate in steam stripping tests utilizing a 3 in. packed column with steam rates of 1 to 2 lb/gal of feed. The investigators did note a tar-like residue on the column packing following the tests.

Solvent extraction of an acidified and a neat sample of retort water was investigated in batch tests using light virgin naphtha. Only 10% of dissolved organic carbon was removed.

Color was removed completely when retort water was contacted with ozone for 60 min. Mild ozonation (5 min) followed by activated sludge treatment demonstrated little or no removal of organic carbon.

Battelle N.W. Laboratories have also conducted a number of treatability screening studies [3]. Steam stripping studies were conducted using a sample of *in-situ* retort water from Utah and a sample of retort water from Lawrence Livermore Laboratory. With the Utah retort water, ammonia removal with recycle of the condensate averaged 90% (initial NH_3 = 3,100 mg/L) for 2 runs at a boiloff rate of 4.5% when condensate was recycled. Over 99% of the ammonia was removed at a boiloff rate of 5.3% when condensate was not recycled. Steam stripping also reduced the alkalinity from 14,300 mg/L to about 4,700 mg/L and the pH of the retort water increased from 8.8 to about 10. Excessive foaming occurred in the reboiler requiring precise liquid level control to prevent the foam from entering the column where it could have caused flooding.

As with the Amoco study, some fouling of the packing in the stripping column was observed. Although settled retort water was used, it contained about 150 mg/L of suspended solids, which were reduced to about 30 mg/L through the stripper. A small volume of light oil was removed by the steam stripping operation. Organic carbon removal by steam stripping ranges from 15% to 20%.

A sample of retort water from the Lawrence Livermore Laboratory (LLL) was steam stripped while operating in the condensate recycle mode at a condensate temperature of 85.5 ± 3.5°C. The ammonia was reduced by 99.5% from 26,500 mg/L to 135 mg/L at a boiloff rate of 15% of the combined feed and condensate recycle. This boiloff rate was equal to 18% of the feed flow alone. Approximately 1/4 of the ammonia was recycled with the condensate stream and 3/4 was evolved from the condensate receiver as a gas. The feed flow to the stripper column with the LLL retort water was restricted to about half that of *in-situ* test site retort water to avoid flooding in the column. Flooding is believed to result from a greater gas flow (CO_2 + NH_3) up the column with the LLL retort water.

Aerobic and anaerobic biological treatability studies were also conducted by Battelle N.W. on five samples of retort water; one retort water sample from the 6,000 kg simulated *in-situ* retort at the Lawrence Livermore Laboratory, one from an above-ground retort in Colorado, and three samples from an *in-situ* test site in Utah. Aerobic treatment consisted of activated sludge or combined trickling filter and activated sludge. The results of the aerobic treatment studies indicated toxicity problems in the treatment units as the concentration of retort water was increased in the feed to the units. Good biological growth and organic carbon removals were observed during the initial phases of the acclimation period, but an apparent toxicity problem develops as the percent actual retort water in the feed increases and the percent artificial retort water decreases. Analysis of the retort water for toxicants revealed the presence of arsenic and thiocyanate. Thiocyanate was not believed to be a problem since the concentration of this constituent was below the threshold value of 500 mg/L for activated sludge; however, arsenic could have been a problem since it exceeded the threshold value of 0.1 mg/L for activated sludge in all samples. Results of anaerobic digestion studies conducted with 3.5 liter digesters also indicated toxicant problems. Gas production from the digesters diminished steadily as the concentration of actual retort water was increased.

Results of studies to evaluate powdered activated carbon addition to the anaerobic digesters indicated successful operation in the case of the Livermore retort water, but continued toxicity problems with the other retort water samples. The activated carbon is also effective in some instances for removing heavy metals from solution in addition to removing organics, but its effect on arsenic in retort water is unknown at the present time. Analysis for soluble arsenic in the digester receiving *in-situ* test site retort water revealed 0.96 mg/L which is near the toxicity threshold for anaerobic digestion. Soluble arsenic in the digester receiving Livermore retort water was 0.56 mg/L. Preliminary results indicate that activated carbon treatment of Utah *in-situ* retort water will permit aerobic biological degradation to take place although the amount of activated carbon needed may be relatively high.

Preliminary stripping and biological treatability tests have also been conducted by Water Purification Associates [3]. Small scale batch stripping tests were conducted by WPA to assist in the design of a larger stripping unit. As with other investigators, WPA found that ammonia and alkalinity stripped simultaneously from a heated sample of retort water. In addition, a minor amount of COD was simultaneously removed. Of significance is the finding that ammonia was not removed after prolonged sparging (16 hr) at an elevated pH at room temperature. Vapor-liquid equilibrium data would predict that some stripping of ammonia should have occurred.

Preliminary results of aerobic treatment experiments indicated that it was possible to successfully treat stripped retort water at pH 7.0 without any dilution. After 70 hr of aeration, 50% of the COD (initial COD > 10,000 mg/L) had been removed; however, the sludge was highly dispersed. WPA isolated excessive pH in the retort water as a toxicant through extensive studies investigating arsenic, cyanide, and pH toxicity. In the successful studies, 5 mL concentrated phosphoric acid was required to bring 1 L of stripped retort water to pH 7.

Yen and Associates have conducted numerous and diverse treatability screening studies focusing on the degradation of organic components in retort water [14]. The technologies investigated include various aerobic and anaerobic biological techniques, electrolytic techniques, and "supplementary techniques" utilizing ozone, permanganate, and photodegradation. In studies of aerobic activated sludge treatment, COD removals of 37% to 43% were observed after 10 days of aeration. Four dilutions of retort water were used in the tests: neat, 4:3, 2:1, and 4:1. No significant difference was observed with the four dilutions in terms of percent COD removal. In order to isolate the organic fractions most inhibitory to biodegradation, the retort water was separated into acidic, neutral, basic, and residual fractions prior to activated sludge treatment. As a result, the basic and residual fractions were found to be most inhibitory.

Preliminary tests with anaerobic treatment of retort water exhibited a 27% removal of COD.

In addition, Yen investigated aerobic treatment with mutant species. In the tests, "phenobac" and "polybac" were used with and without activated sludge. After 21 days, the TOC reduction for the sample with the sludge was 55% and the TOC reduction for the sample without the sludge was 45%.

Preliminary tests with rotating biological contactors were also conducted. Although details of the study are unknown, the data presented indicates poor removal of TOC. Several brief studies with specific bacteria (*Desulforibrio* and *Pseudomonas*) were also conducted, though details of the work are also unknown.

Yen also conducted tests with three electrolytic treatment reactors: a flat-plate cell, a fluidized-bed electrode reactor, and an extended surface electrolytic cell. With the flat-plate cell, 65% reductions in COD were observed. In addition, the effluent supported growth on retort water-agar plates, while the influent did not. The other two systems demonstrated similar results.

As mentioned, several "supplementary" techniques were investigated by Yen. Photodegradation with a tungsten-halogen lamp was demonstrated since peak intensities of highly polar constituents in a liquid chromatogram decreased following treatment. A one-hour treatment with ozone resulted in a 14% reduction in TOC, a 32% reduction in COD, and an 80% reduction in color intensity. Excessive treatment permanganate (13 g/L) results in a 60% reduction of TOC.

The treatability of both process water and retort water with physical/chemical techniques was investigated by Hubbard via bench-scale screening studies [15]. Lime precipitation/stripping, activated carbon treatment, and cationic/anionic exchange were used in various combinations; however, lime treatment → activated carbon treatment → cationic/anionic exchange proved to be the best treatment scheme with both waters. This system provided ~100% removals of ammonium, sodium, carbonate, chloride, and sulfate. The activated carbon step was effective in removing essentially all organic components.

Tests with reverse osmosis were conducted by Osmonics, Inc. with little success in removing TOC [16]. A cellulose acetate membrane with a 600 MW cutoff was used to process 177 liters (47 gallons) of retort water. The RO was operated at 150 psig, and 92% of the retort water was recovered; however, addition of a detergent and a dispersant was necessary to emulsify oils to prevent membrane fouling. RO concentrate was recycled and TOC in the RO permeate averaged 16% less than that of the initial RO feed.

As mentioned, several other key studies in retort water treatability are planned, ongoing, or completed without published report yet available. Of particular interest is the University of Colorado work on wet air oxidation to be published in Industrial Wastes, the Battelle N.W. studies to be detailed in a final report, WPA's work which will be included in a report to be released in late 1980, and evaporator studies conducted by Resource Conservation Company which has received a subcontract from Battelle N.W.

GAS CONDENSATE

No studies concerning the treatability of gas condensate were identified in the literature search. It is expected that gas condensate will be much easier to treat than retort water since no significant concentrations of inorganics other than ammonia, and carbonate species are likely to be present. Oil and grease emulsions may be a problem in gas condensate; however, this phenomena has not been observed. Steam stripping for the removal of ammonia and acid gases should be successful, since its success has been demonstrated with retort water--a much more contaminated stream. Steam stripping should also remove some or all organics which may be present, though this has not been demonstrated. Many treatment options, as discussed in Section 3 exist if organics remain in the stripper effluent.

LEACHATE

As with gas condensate, no studies concerning the treatability of leachate were identified in the literature search. In addition, it is difficult to speculate as to which treatment systems would treat leachate since only limited characterization data is available. If leachate is a major wastewater stream from surface retorting operations, it is expected that at least treatment for TDS and trace metals will be required prior to leachate discharge.

DISCUSSION

Several treatability screening studies have been conducted to fill many treatment step needs identified in Figures 6 through 8, particularly in the case of mine water and retort water treatment. Because of their design and intent, these studies have generally been useful to screen potential technologies and eliminate others. Many key technical questions still remain unanswered such as:

- How should emulsified oil be separated in retort and product water?
- What is the best system for removal of organics from retort and product water?
- Will state-of-the-art technologies treat gas condensate and leachate?

To answer these questions, and to size pilot-plant equipment, MRC recommends conducting additional bench-scale treatability studies. Presently, there are several opportunities for MRC to obtain

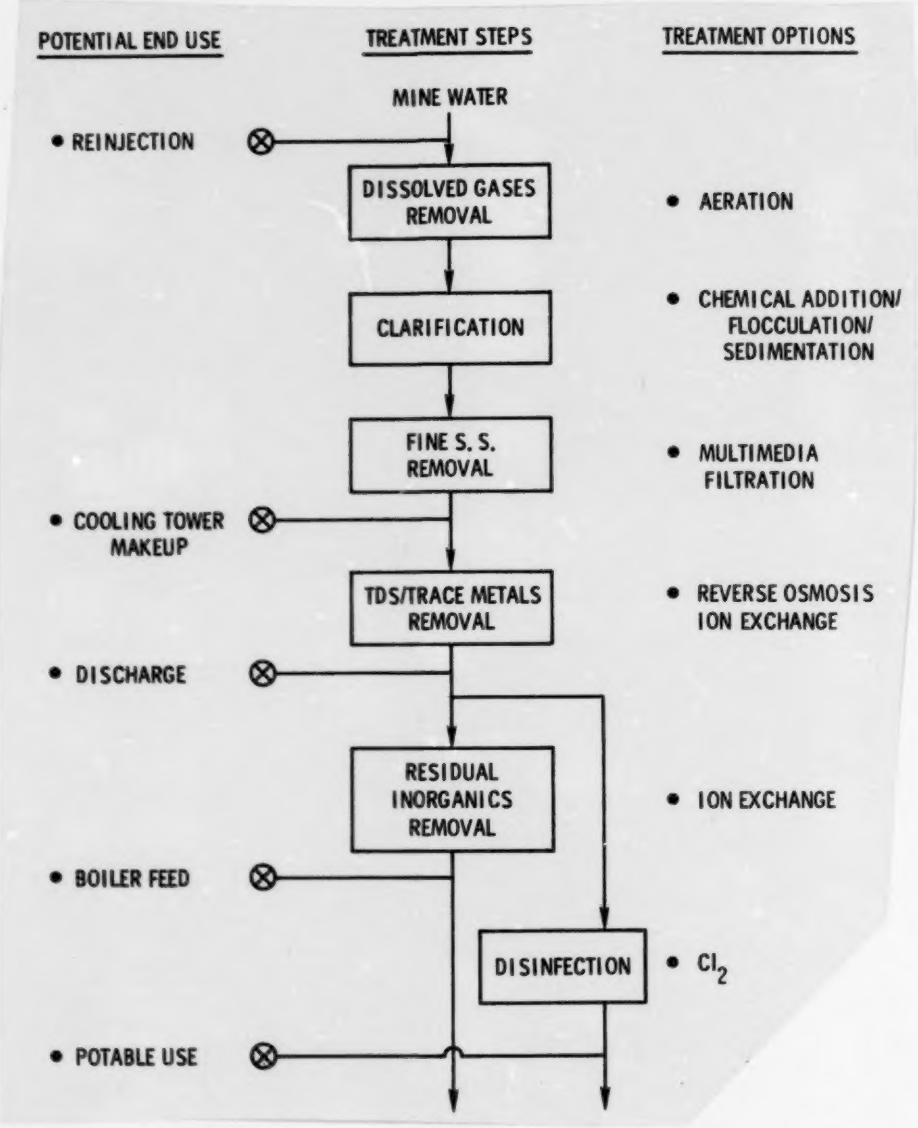
POTENTIAL END USE
TREATMENT STEPS
TREATMENT OPTIONS
MINE WATER
• REINJECTION
DISSOLVED GASES REMOVAL
• AERATION
CLARIFICATION
• CHEMICAL ADDITION/ FLOCCULATION/ SEDIMENTATION
FINE S. S. REMOVAL
• MULTIMEDIA FILTRATION
• COOLING TOWER MAKEUP
TDS/TRACE METALS REMOVAL
• REVERSE OSMOSIS ION EXCHANGE
• DISCHARGE
RESIDUAL INORGANICS REMOVAL
• ION EXCHANGE
• BOILER FEED
DISINFECTION
• Cl_2
• POTABLE USE

Figure 6. Mine water treatability options.

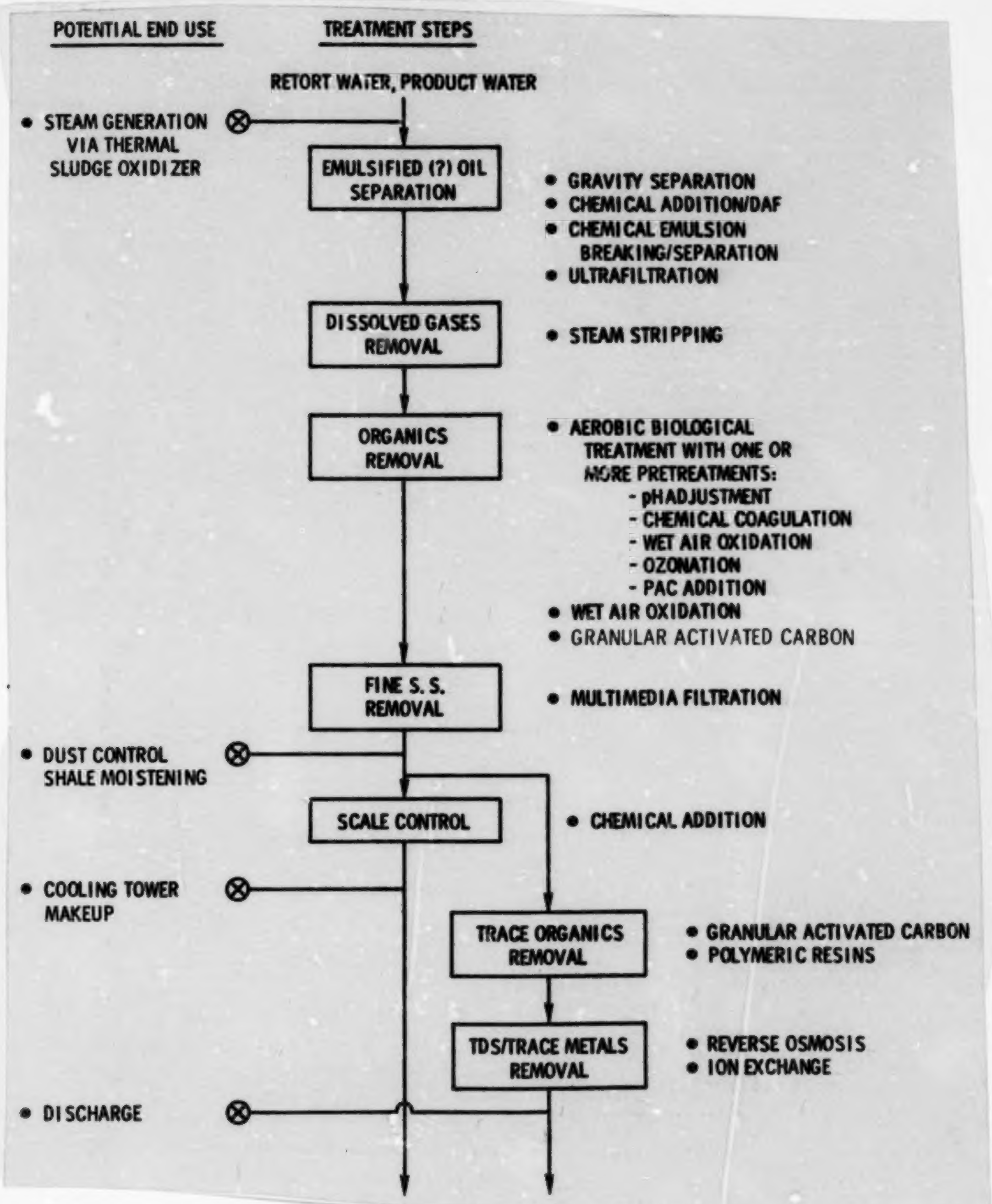
POTENTIAL END USE
TREATMENT STEPS
RETORT WATER, PRODUCT WATER
• STEAM GENERATION VIA THERMAL SLUDGE OXIDIZER
EMULSIFIED (?) OIL SEPARATION
• GRAVITY SEPARATION
• CHEMICAL ADDITION/DAF
• CHEMICAL EMULSION BREAKING/SEPARATION
• ULTRAFILTRATION
DISSOLVED GASES REMOVAL
• STEAM STRIPPING
ORGANICS REMOVAL
• AEROBIC BIOLOGICAL TREATMENT WITH ONE OR MORE PRETREATMENTS:
- pH ADJUSTMENT
- CHEMICAL COAGULATION
- WET AIR OXIDATION
- OZONATION
- PAC ADDITION
• WET AIR OXIDATION
• GRANULAR ACTIVATED CARBON
FINE S. S. REMOVAL
• MULTIMEDIA FILTRATION
• DUST CONTROL SHALE MOISTENING
SCALE CONTROL
• CHEMICAL ADDITION
• COOLING TOWER MAKEUP
TRACE ORGANICS REMOVAL
• GRANULAR ACTIVATED CARBON
• POLYMERIC RESINS
TDS/TRACE METALS REMOVAL
• REVERSE OSMOSIS
• ION EXCHANGE
• DISCHARGE

Figure 7. Retort wastewater treatability options.

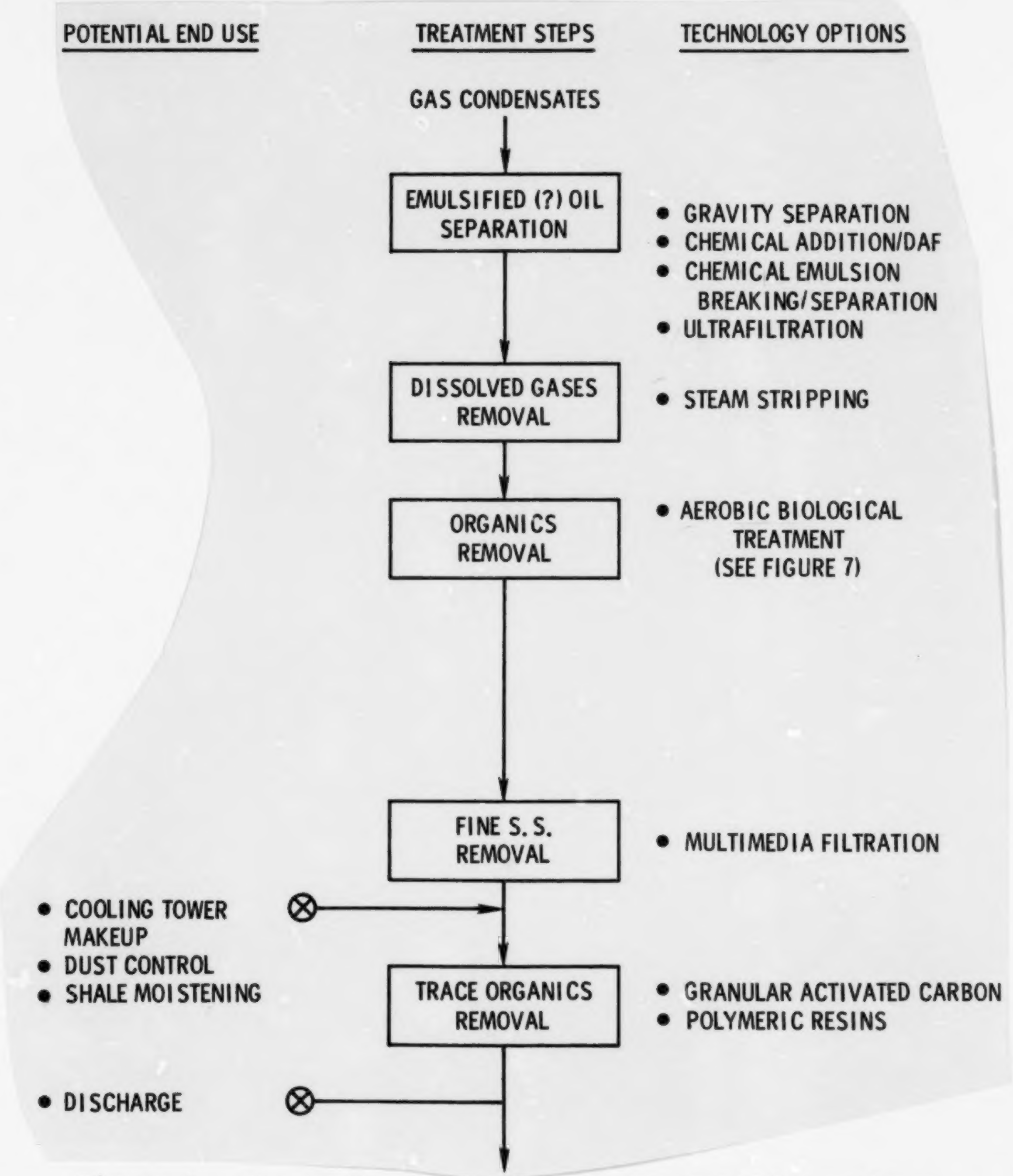
POTENTIAL END USE
TREATMENT STEPS
TECHNOLOGY OPTIONS
GAS CONDENSATES
EMULSIFIED (?) OIL SEPARATION
• GRAVITY SEPARATION
• CHEMICAL ADDITION/DAF
• CHEMICAL EMULSION BREAKING/SEPARATION
• ULTRAFILTRATION
DISSOLVED GASES REMOVAL
• STEAM STRIPPING
ORGANICS REMOVAL
• AEROBIC BIOLOGICAL TREATMENT (SEE FIGURE 7)
FINE S.S. REMOVAL
• MULTIMEDIA FILTRATION
• COOLING TOWER MAKEUP
• DUST CONTROL
• SHALE MOISTENING
TRACE ORGANICS REMOVAL
• GRANULAR ACTIVATED CARBON
• POLYMERIC RESINS
• DISCHARGE

Figure 8. Gas condensate wastewater treatability options.

relevant samples of retort wastewaters with which to conduct these studies, namely:

- Rio Blanco - mine water and retort water
- Tosco - gas condensate
- Geokinetics - retort water
- Occidental - retort water and gas condensate

In the case of mine water treatment, only Battelle N.W. has conducted bench-scale treatability studies for the removal of fluoride and boron which are of primary concern if the excess mine water is to be discharged or used for potable purposes. Activated alumina absorption and precipitation with phosphoric acid and lime were identified as promising technologies for the removal of boron. WPA reported that electrodialysis and reverse osmosis could produce a more than adequate effluent; however, reverse osmosis appears to be more cost-effective at the high TDS levels expected and has added technical advantages.

Therefore, additional research is needed to demonstrate the feasibility of reverse osmosis treatment of mine water and to size pilot-plant equipment in the case of other treatment steps. Suggested technology options to be investigated in these studies are listed in Figure 6.

Many more studies have been conducted with retort water; however, key technical questions remain. For example, no studies have been conducted to investigate emulsified oil separating from retort and product water. Steam stripping has been identified by several investigators as the best technology for dissolved gases removal, though they have experienced fouling of column packings. Emulsified oil separation may alleviate the problem. Many studies have been conducted to assess technologies for organics removal, though many questions remain. Aerobic biological treatment has classically been the most cost-effective method of organics removal from municipal wastes, but it has been found that various pretreatments are required for these systems to operate with retort water. In addition, a large portion of the organics (∿50%) appear to be refractory. Therefore, additional studies are needed to identify methods which would enhance the ability of aerobic biological treatment to remove organic compounds. The sensitivity of biological systems to variations in retort water composition has serious implications for commercial operations. If it is found that wastewater cannot be treated biologically, it may become necessary to test physical/chemical methods such as wet air oxidation and granular activated carbon adsorption. It is unlikely that retort water would be discharged from a full-scale retorting facility; however, if discharge is necessary, treatment for trace organics, trace metals, and TDS will become necessary. Several investigators have used granular activated carbon and polymeric resins for gross organics removal; however, studies are needed to assess these technologies for their ability to remove refractory organics present in the effluent from the gross organics removal treatment step. Studies of TDS and trace metals removal by reverse osmosis and ion exchange would also become necessary.

Suggested treatment options to treat retort water to discharge quality are shown in Figure 7.

As pointed out in Section 3, treatment to discharge quality will probably not be necessary in full scale systems since many in plant uses for retort water are envisioned. Bench-scale studies conducted at this time are still recommended to complete a retort treatability data base which would be used by industry and government in making water use decisions.

No known studies exist for the treatment of gas condensate, though, this stream should not be difficult to treat, compared to retort water. At this time, the extent to which emulsions are present in gas condensate is not known. If present, they will have to be removed prior to subsequent treatment steps. Steam stripping studies are necessary to assess organics removal as well as inorganic dissolved gases removal. If organics remain following steam stripping, studies for their removal will have to be initiated. Suggested technology options for gas condensate treatment are listed in Figure 8.

Since it is not known whether leachate from spent shale piles will be present in significant quantities, and leachate quality is still not fully understood, research funds should be directed to address these issues rather than investigating treatment alternatives. If spent shale piles are found to be porous, and the leachate from percolation through the piles is toxic or unacceptable for groundwater discharge, serious questions about leachate collection in full-scale systems exist.

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APPENDIX A

OIL SHALE RETORTING PROCESSES

SURFACE RETORTING PROCESSES

Paraho Process

Process Description [17]--
The Paraho process is a developmental outgrowth of the Gas Combustion Retort, developed by the U.S. Bureau of Mines in 1951 at Anvil Points, Colorado [17].

The Paraho Process may be operated in one of two modes, gas combustion or hot inert gas retorting. The gas combustion mode is a direct process and is depicted in Figure A-1. In this mode, shale is introduced into the top of the retort through a rotating spreader, passes through 4 zones, and is discharged through a special, hydraulically operated discharge grate, which more uniformly controls solids flow rates. Retort off-gases (approximately 3.8 x 10^6 J/cm^3 or 100 Btu/SCF) are recycled to the retort at three points. These gases, together with combustion of a portion of the carbonaceous residue on the spent shale, provide the heat for the process. The retorted shale containing a 2.3% carbonaceous residue, is discharged to disposal at approximately 150°C (300°F). Retort gases, oil mist, and vapors leave the top of the retort at approximately 150°F (65.5°C), and pass through a cyclone, wet electrostatic precipitator, and aerial condenser to remove oil. As previously noted, a portion of these gases are recycled to the retort.

The Paraho process may also be operated in hot inert gas, or indirect mode (Figure A-2), in which case no combustion is carried out in the retort, per se. The retort gases therefore have a high heating value of 3.4 x 10^7 (900 Btu/SCF). A portion of these gases are used to heat a recycle portion of the gas in an external furnace, and the latter are recycled to the retort as a heat source. The retorted shale has a carbon content of 4.5%. A combination of direct and indirect operating modes may also be employed.

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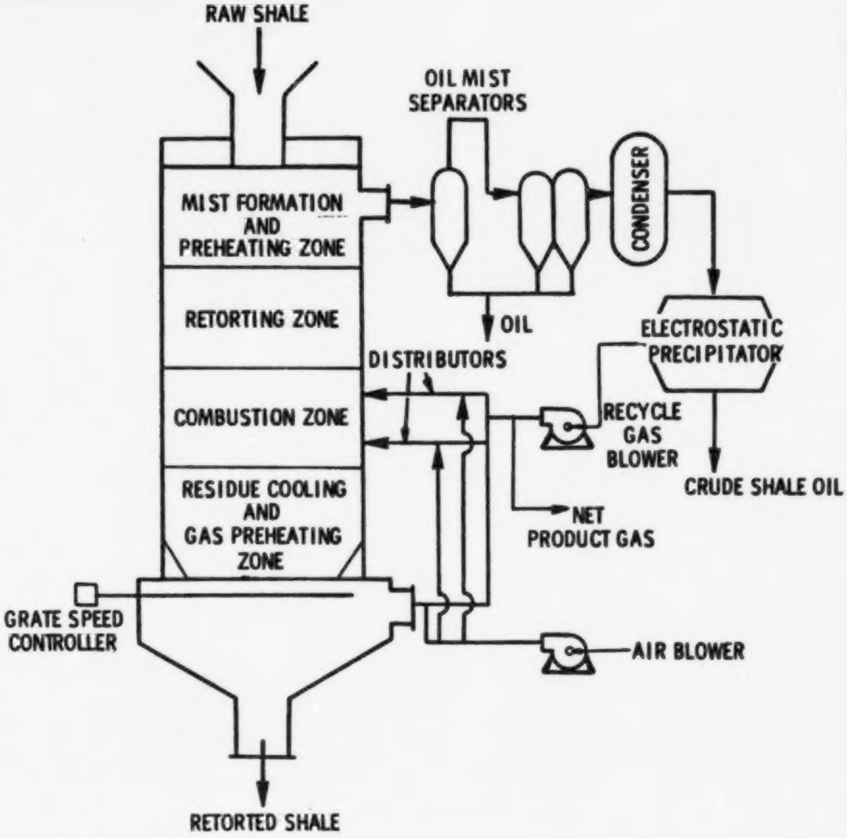
RAW SHALE
OIL MIST SEPARATORS
CONDENSER
MIST FORMATION AND PREHEATING ZONE
RETORTING ZONE
OIL
ELECTROSTATIC PRECIPITATOR
DISTRIBUTORS
COMBUSTION ZONE
RECYCLE GAS BLOWER
CRUDE SHALE OIL
RESIDUE COOLING AND GAS PREHEATING ZONE
NET PRODUCT GAS
GRATE SPEED CONTROLLER
AIR BLOWER
RETORTED SHALE

Figure A-1. Schematic of Paraho direct mode gas combustion retorting process [17].

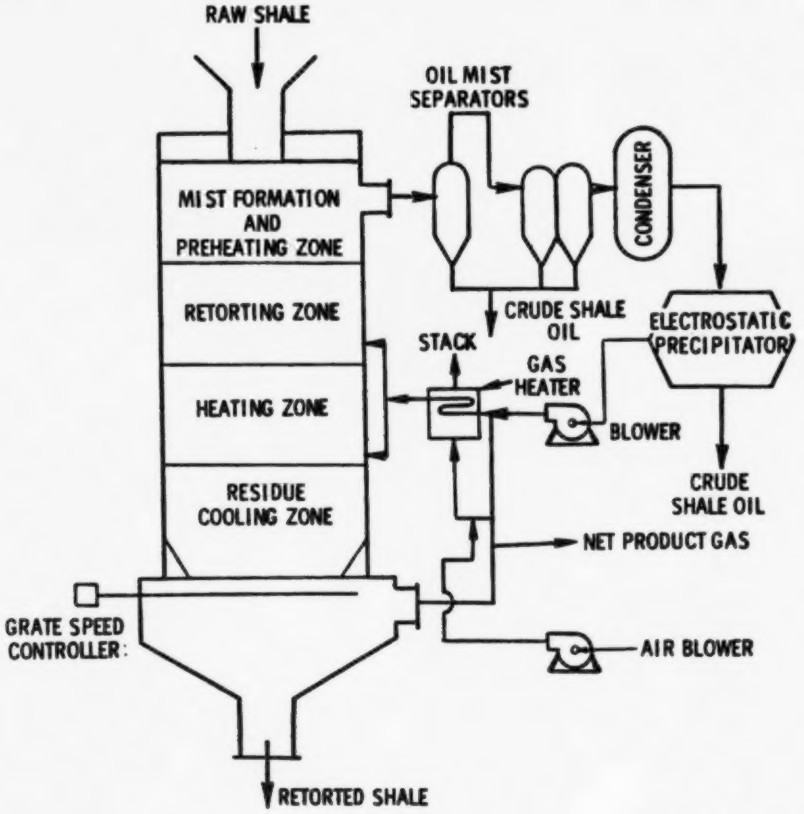
RAW SHALE
OIL MIST SEPARATORS
MIST FORMATION AND PREHEATING ZONE
CONDENSER
RETORTING ZONE
CRUDE SHALE OIL
ELECTROSTATIC PRECIPITATOR
STACK
GAS HEATER
HEATING ZONE
BLOWER
CRUDE SHALE OIL
RESIDUE COOLING ZONE
NET PRODUCT GAS
GRATE SPEED CONTROLLER
AIR BLOWER
RETORTED SHALE

Figure A-2. Schematic of Paraho indirect mode hot inert gas retorting [17].

Various upgrading processes may also be present at the retorting site. These include delayed coking followed by hydrogenation of the naphtha and gas oil fractions. The products of this process are a clean crude shale oil, ammonia, sulfur and coke [18].

Process Use

The Paraho process is intended for use at the White River project and is presently being used by the developer, Paraho Development Corporation at Anvil Points, Colorado. Development of the Paraho processes began in 1972 when Development Engineering, Inc., a subsidiary of Paraho Development Corporation, obtained a lease from the Department of the Interior to conduct surface oil shale retorting at Anvil Points, Colorado [19]. In late 1973, with funds provided by 17 participating companies, two Paraho oil shale retorts were constructed. One was a small pilot-plant to investigate operating parameters, and the other was a 410-Mg (450-ton)/day semiworks for large-scale testing under production conditions [19]. The semiworks retort was operated successfully in both the direct and indirect modes of heating by February 1976 [19]. At that time, the Office of Naval Research and the Energy Research and Development Administration (now DOE) awarded Paraho a \$13-$\bar{M}$ contract to produce 15,900 m^3 (100,000 bbl) of shale oil for refining tests [20]. The program was completed last year [21]. In January 1977, a draft environmental impact statement was submitted for Paraho's proposed full-size commercial retorting facility [22], which was designed to process 11,800 Mg (13,000 tons)/day of raw shale [19]. Paraho initiated Phase I of the three-phase, 5-year, \$92-$\bar{M}$ program at its own expense on December 1, 1977 [23].

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[19] Shih, C. C., J. E. Cotter, C. H. Prien, and T. D. Nevens. Technological Overview Reports for Eight Oil Shale Recovery Processes. EPA-600/7-79-075, U.S. Environmental Protection Agency, Cincinnati, Ohio. March 1979. 115 pp.

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[23] Paraho Announces Three-Phase Module Program. Synthetic Fuels, 15(1):2-3 through 2-10, March 1978.

The present semiworks at Anvil Points is larger than a pilot-plant but smaller than a commercial scale facility and is depicted in Figure A-3. In addition to the retort, supportive process equipment includes raw shale crushers, condensers for oil shale vapor and product gas, a precipitator, various blowers for air, recycle and product gas, water storage and treatment facilities and spent shale disposal equipment [24].

The Paraho process is also intended for use at the White River Shale project to retort coarse rubblized shale, while fines will be retorted in TOSCO II retorts [10]. Planned use of the Paraho process was indicated on July 1, 1976, when the White River Shale Oil Corporation submitted a Detailed Development Plan calling for the use of both types of Paraho retorting technology to process 85% of the shale mined from Tracts U-a and U-b in Uintah County, Utah [25]. However, exactly one year later, a court injunction suspended White River's leases due to questions of property ownership, specifically unpatented pre-1920 oil shale placer mining claims and an application by Peninsula Mining Company for a Utah state lease to the same property [26]. Therefore, development of Tracts U-a and U-b by White River will be delayed for several years pending resolution of the legal issues [26] (personal communication, Rees C. Madsen, White River Shale Oil Corporation, to Gerald M. Rinaldi, Monsanto Research Corporation, August 17, 1979).

The project activities planned for Tracts U-a and U-b are expected to occur in four phases. In Phase I a 335 meter (1,100 ft) deep access shaft for a subsequent room-and-pillar mine will first be established near the center of the combined tracts, in order to permit testing of the shale deposit. Mining will be initiated some six months later. Mine development will continue, and extend throughout the following Phase II, with an expansion of production from 1.814×10^6 kg (2,000 tons) to 9.10×10^6 kg (10,000 tons) of raw shale per day.

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[24] Compendium Reports on Oil Shale Technology, Slawson & Yen, EPA-600/7-79-039, January 1979.

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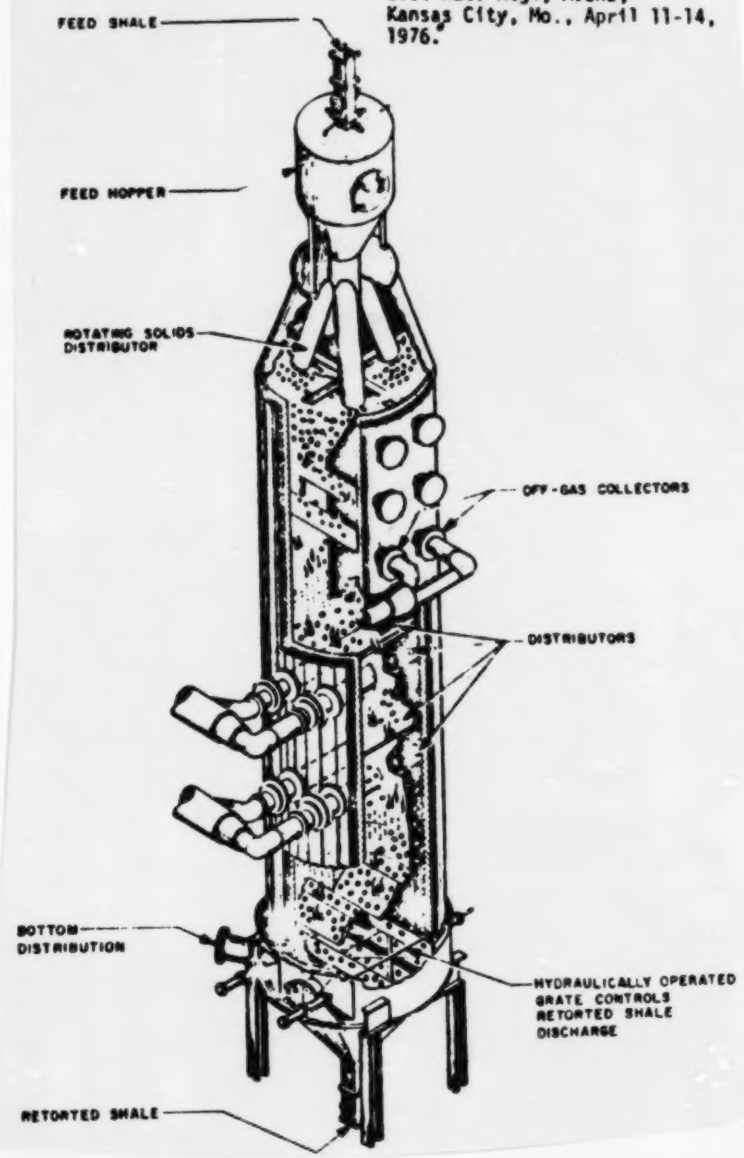

*from Jones, John B., "The Paraho Oil Shale Retort, 81st Nat. Mtg., AIChE, Kansas City, Mo., April 11-14, 1976."

FEED SHALE
FEED HOPPER
ROTATING SOLIDS DISTRIBUTOR
OFF-GAS COLLECTORS
DISTRIBUTORS
BOTTOM DISTRIBUTION
HYDRAULICALLY OPERATED GRATE CONTROLS RETORTED SHALE DISCHARGE
RETORTED SHALE

Figure A-3. The Paraho retort.

Phase II will be of four years duration, and will involve the construction and operation of a single modular vertical retort with a throughput capacity of up to 9.10 x 10^6 kg of shale (10,000 tons) per day. The retort design has not yet been selected, but could be a Paraho direct-heat design later modified for indirect heating, or another available vertical-type retort. At a retort feed rate of 6.80 x 10^6 kg (7,500 tons) of coarse shale per day, some 750 cubic meters (4,700 barrels) of crude oil would be produced daily.

A commercial plant (Phase III), with a first "train" projected capacity of 7.25 x 10^7 kg (80,000 tons) per day, will be constructed for start-up some 2 1/2 years after the successful conclusion of Phase II. This will be followed by start-up of a second commercial train of the same capacity some 1 1/2 years after the first, thus bringing total plant production capacity to an ultimate 1.45 x 10^8 kg (160,000 tons) per day.

It is currently intended that the major portion (85%) of the Phases III and IV retorting will be carried out in vertical, gas-combustion type, direct and indirect-mode retorts, but that the 15% of crushing fines produced will be pyrolyzed in TOSCO II-type retorts. It is expected that all of the 15,800 cubic meters (100,000 barrels) of shale oil produced daily at maximum scale-up will be upgraded in facilities similar to those to be used for the Colony and Tract C-b projects.

Water Quality/Quantity Data--

A conceptual water flow diagram of a Paraho surface retort oil shale facility as designed by WPA is shown in Figure A-4. It is envisioned that water resulting from retorting will ultimately be used as cooling water makeup following ammonia/acid gas stripping, organics removal, and clarification. Blowdown from the cooling tower will then be used in spent shale moisturizing with no treatment requirements.

Available water quality data is listed in Tables A-1 through A-4.

Tosco II Process

Process Description [17]--

The TOSCO II process originated as the Aspeco process which The Oil Shale Corporation (TOSCO) purchased from Aspergren and Company of Stockholm, Sweden in 1952. Under TOSCO sponsorship, initial development work was conducted from 1955 to 1966 by the Denver Research Institute using a 24 ton/day pilot-plant.

In the TOSCO II process, minus one-half inch crushed shale (including fines) is preheated by direct contact with hot flue gases from a ball heater (see Figure A-5) used downstream in the process. The preheated shale is then fed to a horizontal, rotating retort, where it is heated to 482°C (900°F) by mixing with small, hot

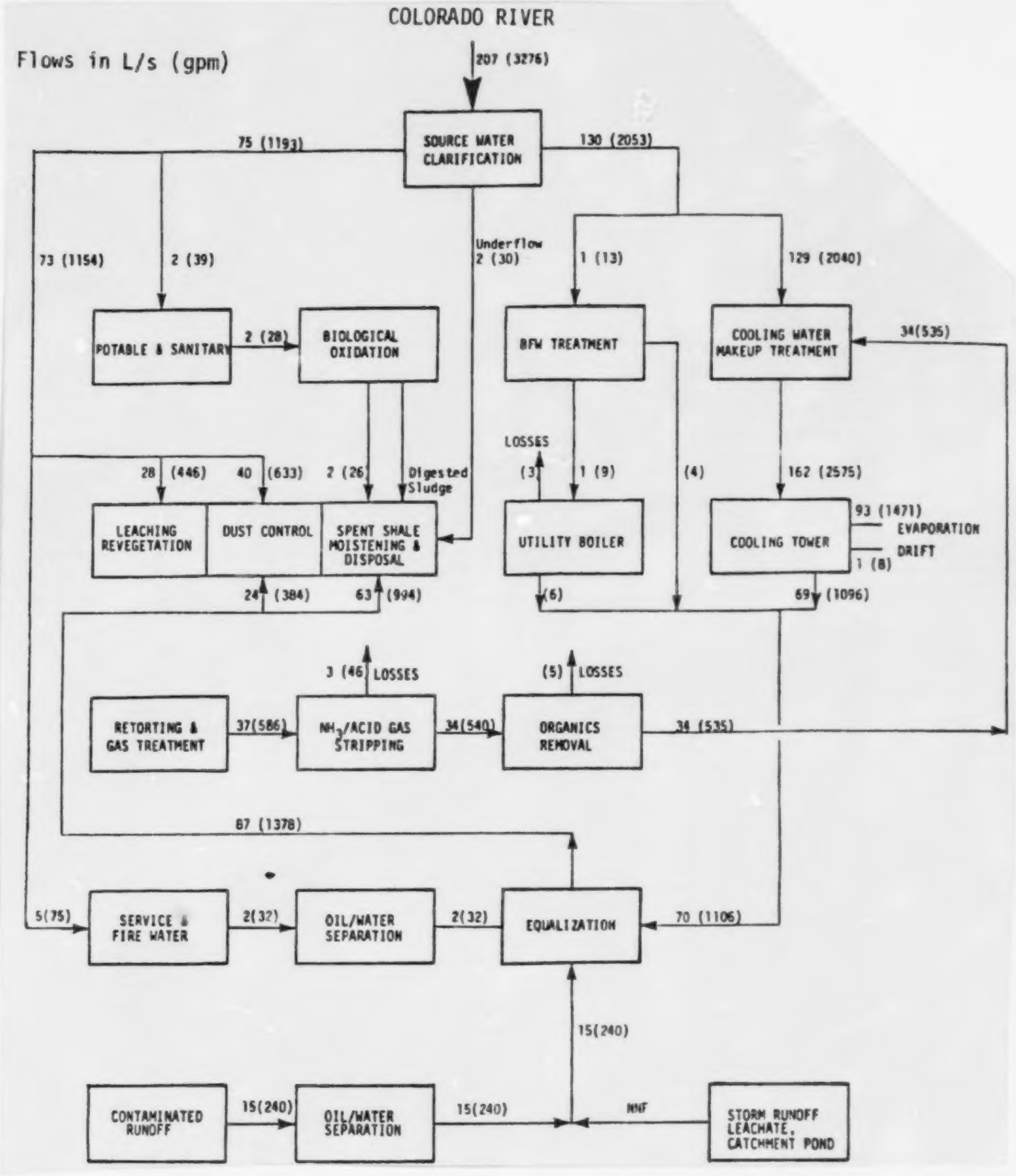
COLORADO RIVER
Flows in L/s (gpm)
207 (3276)
SOURCE WATER CLARIFICATION
75 (1193)
130 (2053)
73 (1154)
2 (39)
Underflow 2 (30)
1 (13)
129 (2040)
POTABLE & SANITARY
2 (28)
BIOLOGICAL OXIDATION
BFW TREATMENT
COOLING WATER MAKEUP TREATMENT
34(535)
LOSSES
28 (446)
40 (633)
2 (26)
Digested Sludge
(3)
1 (9)
(4)
162 (2575)
LEACHING REVEGETATION
DUST CONTROL
SPENT SHALE MOISTENING & DISPOSAL
UTILITY BOILER
COOLING TOWER
93 (1471)
EVAPORATION
DRIFT
1 (8)
24 (384)
63 (994)
(6)
69 (1096)
3 (46) LOSSES
(5) LOSSES
RETORTING & GAS TREATMENT
37(586)
NH3/ACID GAS STRIPPING
34(540)
ORGANICS REMOVAL
34 (535)
87 (1378)
5(75)
SERVICE & FIRE WATER
2(32)
OIL/WATER SEPARATION
2(32)
EQUALIZATION
70 (1106)
15(240)
CONTAMINATED RUNOFF
15(240)
OIL/WATER SEPARATION
15(240)
NNF
STORM RUNOFF LEACHATE, CATCHMENT POND

Figure A-4. Major water streams for Paraho direct heated process producing 15,900 m^3/day (99,170 BPSD) crude shale oil [27].

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[27] Hicks, R. E. and R. F. Probstein. Water Management in Surface and *In-Situ* Oil Shale Processing. Presented at the 87th Meeting of AIChE. Boston, Massachusetts, August 1979.

TABLE A-1. CHARACTERIZATION OF SOURCE WATER STREAMS - PARAHO PROCESS mg/L

Species	Source water Colorado River [28, 29]	Source water[a] [24]	Clarified source water[b] as $CaCO_3$ [28]	Clarified source water[a,c] [24]	Cooling tower makeup as $CaCO_3$[d] [28]	Boiler feed water[a,e] [24]
Alkalinity		150 - 250[f]		150 - 250[f]		<5
COD						nil
Hardness		200 - 350[f]		200 - 350[f]		<5
Oil and grease (total)		0 - 5		nil		nil
TDS	734	400 - 800		400 - 800		50 - 100
Solids (suspended)		300 - 1,000		20 - 50		nil
Ammonia		<1		<1		nil
Phenols		<1		<1		nil
SiO_2	7.0					
Bicarbonates	168.0		137.8 and 124.3		37.3	
Chloride	205		289.0		289.0	
Nitrate	8.6		7.0		7.0	
Phosphate (total)		0 - 1[g]		0 - 1[g]		nil
Sulfate	158.0		164.3 and 177.8		264.7	
Calcium	72.0		179.3		179.3	
Magnesium	19.0		77.9		77.9	
Potassium	5.3		6.8			
Sodium	145.0[h]		334.1[h]		334.1	
pH	7.4				5.8[i]	

[a] Estimated data for White River Shale Project where Paraho technology will be used to retort rubblized shale, and Tosco II technology will be used to retort fines.

[b] Following 30 ppm alum dosage and clarifications.

[c] Following sedimentation and filtration.

[d] After neutralization of 80% alkalinity with H_2SO_4.

[e] Clarified source water following ion exchange and deaeration.

[f] mg/L $CaCO_3$.

[g] mg/L as PO_4.

[h] Adjusted by 18.0 mg/L as $CaCO_3$ for ionic balance.

[i] pH 7 in circulating cooling water.

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[28] Predicted Cost of Environmental Controls for a Commercial Oil Shale Industry, Denver Research Institute. Prepared under U.S. Department of Energy contract No. EPA-78-S-02-5107.

[29] Quality of Surface Water of the United States, Parts 9 & 10. USGS, 1970. p. 33.

TABLE A-2. CHARACTERISTICS OF WASTEWATER STREAMS - PARAHO PROCESS mg/L

Species	Recycle gas condensate [30]		Gas condensate [31, 32]	Recycle gas condensate indirect mode	Process water separated from product oil [33]	Process water separated from product oil [32]	Process water separated from product oil direct mode [30]
	Direct mode	Indirect mode					
Alkalinity (total)	68,550	12,900	22,200		5,900 - 35,200	24,700	
BOD	12,000	4,850			75,000		
COD	19,400	17,100	1,730		17,000 - 66,400	75,700	
Carbon (total)			7,190			40,700	
TIC	9,800	1,600					
TOC	29,200	9,800	5,010		1,060 - 19,300	32,800	
Hardness	152	98					
TKN	31,400				4,600 - 33,600		
Nitrogen (total)			5,410			25,900	
Oil and grease (total)	502	33.3			900 - 964		
Sulfur (total			1,540	3		43,200	>10
Solids (total)	22,000	429					
TDS			8.2		17,400 - 160,000	157	
Solids (suspended)	200		4.5		137,000 - 700	84	
Solids, volatile					137,000 - 159,700		
Ammonia	14,060	16,800	6,470^a			32,500^a	
Chlorine			0.4				2.0
Fluorine				0.1			7
Phosphorus				0.2			5.0
Bicarbonate	31,265	6,280			1,500		
Bromine				0.02			0.009
Carbonate	30,500	3,030	7,960^b		0	28,900^b	
Chloride	trace	trace	390		1,550 - 70,000	1,740	
Cyanide			32.7		<0.001 - 0.1	5.2	
Fluoride	0.35	0.00	0.50		5 - 19	1.96	
Iodine				0.008			
Nitrate	118	1.0	<0.1		2,570		
Nitrite	0.02	<0.002			0.3		
Phosphate (total)	0.058	0.75			<1.5 - 33		
Sulfate	113.6	1.65	930		210 - 5,900	9,140	
Sulfite	0.1	390	<0.1		<0.001 - 0.5	ND	
Aluminum				0.2	2.4 - 4.6		0.8
Ammonium	5,652	13,540			830 - 4,080		
Arsenic			<2	0.09	<0.005	9.0	1.0
Barium				0.1	<3		2.0
Boron			<20	0.6	1.2 - 10	35.0	5.0
Calcium	60.7	39.2	12.4	8	18 - 76	37.9	>10
Cesium				0.01			0.01
Chromium			<0.005	0.07	0.3	0.11	0.3
Cobalt				<0.01	0.15		<0.04
Copper			<0.07	0.1	0.04 - 9	1.34	0.2
Gallium				0.04			<0.02

(continued)

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TABLE A-2 (continued)

Species	Recycle gas condensate [30] Direct mode	Recycle gas condensate [30] Indirect mode	Gas condensate [31, 32]	Recycle gas condensate indirect mode	Process water separated from product oil [33]	Process water separated from product oil [32]	Process water separated from product oil direct mode [30]
Germanium							<0.05
Iron			1.6	>10	2.2 - 7	6.45	5.0
Lead			<1	0.07	0.33 - 3	2.25	0.2
Lithium				0.02	<2		1.0
Magnesium	<0.1	<0.1	25	3	30 - 200	540	>10
Manganese				0.2			0.3
Mercury			<7	<0.01	1.2	13.5	<0.01
Molybdenum			<2	0.3	<0.2 - 0.43	1.85	0.1
Nickel				0.1	<2		0.2
Potassium	0.08	0.18	1.5	3	3 - 35	25.3	>10
Praseodymium				0.008			
Rubidium				0.4			
Scandium				0.01			<0.05
Selenium			1	0.04		12.5	0.1
Silicon			4.0	4	3 - 3.5	32.0	>10
Sodium	0.2	0.29	35.5	5	30 - 290	278	>10
Strontium				0.1	0.6		3.0
Tin				0.05	<0.3		
Titanium				0.9	<0.2		0.3
Uranium				0.03			
Vanadium				<0.01	<0.3		0.03
Yttrium				0.007			
Zinc			0.02	0.2	1.2	0.82	0.4
Zirconium				0.05			
Phenols	46	42	43.1		8.7 - 19	4.06	
pH	9.8	9.5	9.0		7.6 - 8.6	8.45	
Cadmium			<0.05		<0.005 - 0.9	0.22	
Silver			0.8		0.6	0.3	
Lanthanum				0.04			
Antimony					<0.9		

[a]As N.

[b]As CO_2.

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[30] Cotter, J. E., C. H. Prien, J. J. Schmidt-Collerus, D. J. Powell, R. Sung, C. Habenicht, and R. E. Pressey, Sampling and Analysis Research Program at the Paraho Oil Demonstration Plant, U.S. Environmental Protection Agency contract 68-02-1881, 1977.

[31] Atwood, R. A., and R. N. Heistand. Environmental Evaluations Paraho Operations. Final Technical Report, Development Engineering, Inc., September 1978.

[32] Laramie Energy Technology Center Process Effluent Evaluation. Prepared by Science Application for U.S. Environmental Protection Agency under contract No. 31-109-38-3764, May 1979.

[33] Draft Environmental Impact Assessment for a Proposed Accelerated Paraho Oil Shale Research Project at Anvil Points, Colorado. U.S. Bureau of Mines, May 1975.

TABLE A-3. CHARACTERISTICS OF OTHER WASTEWATER STREAMS - PARAHO PROCESS
mg/L

Species	Service water[a] [34]	Sanitary wastewater[a] [34]	Blowdowns[a,b] [34]	Spent shale leachate[c] [35]
TOC				400
BOD	50 - 500	20		
COD	100 - 2,000	50		
Oil and grease	50 - 1,000	<5		
TDS	500 - 2,000	1,000 - 2,000	5,000 - 10,000	37,000
Solids (suspended)	30 - 500	30	100 - 500	
Phenols		<1		
SiO_2				46.7
Bicarbonate				29.4
Chloride				2,300
Fluoride				19.7
Nitrate				<0.1
Sulfate				20,200
Aluminum				0.16
Arsenic				0.15
Barium				0.24
Beryllium				0.007
Boron				2.99
Calcium				527
Chromium				0.02
Copper				0.32
Iron				0.29
Lead				0.042
Magnesium				202
Manganese				0.26
Molybdenum				9.45
Nickel				0.04
Potassium				1,460
Selenium				0.04
Silver				0.004
Strontium				13.6
Vanadium				0.45
Zinc				1.09
Sodium				10,400

[a] Estimated data for White River Shale Project where Paraho Technology will be used to retort rubblized shale, and Tosco II technology will be used to retort fines.

[b] From cooling tower, steam generator and spent ion exchange reagent.

[c] Maximum concentrations observed in a series of tests utilizing various soil cover thicknesses and lysimeter slopes.

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[34] Whie River Oil Shale Project, Detailed Development Plan, Volume I.

[35] Harbert, Berg, and McWhorter. Lysimeter Study on the Disposal of Paraho Retorted Oil Shale. EPA-600/7-79-188.

TABLE A-4. CHARACTERISTICS OF TREATED WASTE-WATER STREAMS - PARAHO PROCESS
mg/L

Species	Foul water stripper effluent[a,b] [34]	Treated stripper effluent/service water[a,c] [34]
BOD		150 - 250
COD	500 - 1,500	
Oil and grease	50 - 100	20 - 50
TDS		800 - 1,000
Solids (suspended)		200 - 300
Ammonia	25 - 50	10 - 15
Phenols	80 - 150	<1
Phosphate (total)		5 - 10

[a] Estimated data for White River Shale Project where Paraho technology will be used to retort rubblized shale, and Tosco II technology will be used to retort fines.

[b] Stripper treating various gas and oil upgrading, and retort wastewater streams.

[c] Following flotation and biological oxidation.

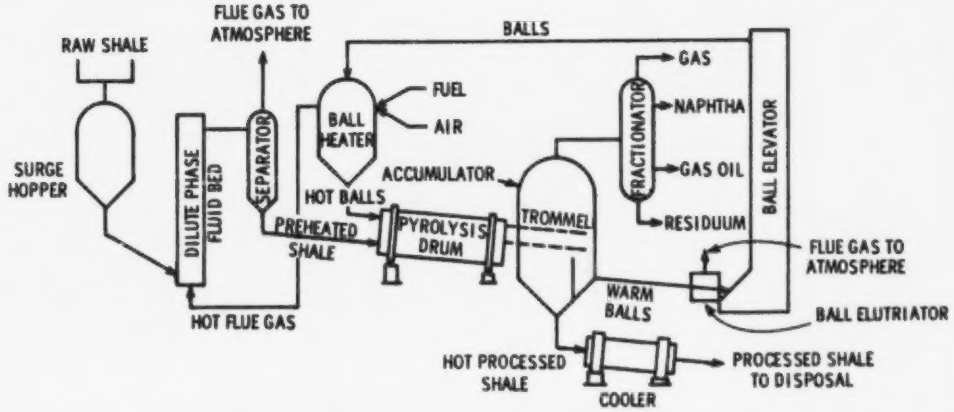
RAW SHALE
FLUE GAS TO ATMOSPHERE
BALLS
GAS
FUEL
AIR
NAPHTHA
SURGE HOPPER
DILUTE PHASE FLUID BED
SEPARATOR
BALL HEATER
FRACTIONATOR
BALL ELEVATOR
ACCUMULATOR
GAS OIL
HOT BALLS
TROMMEL
RESIDUUM
PREHEATED SHALE
PYROLYSIS DRUM
FLUE GAS TO ATMOSPHERE
WARM BALLS
HOT FLUE GAS
BALL ELUTRIATOR
HOT PROCESSED SHALE
COOLER
PROCESSED SHALE TO DISPOSAL

Figure A-5. Schematic of the TOSCO II Retorting Process [17].

ceramic balls. Shale oil vapors are removed, fractionated, and condensed. The cooled balls and retorted (spent) shale are discharged from the retort and screened to separate the spent shale from the balls. The spent shale is cooled in a rotating drum steam generator, moistened to about 14% water content, and transported to the disposal site. As discarded, it normally contains about 4% to 5% residual carbonaceous matter.

The cooled balls are sent to an external ball heater, reheated, and recycled to the retort. In a typical situation, the ball to raw shale feed ratio to the retort is about 2:1. The ball heater can use an outside fuel, a portion of retort off-gases, and/or even the carbonaceous residue on the spent shale as a fuel source(s).

The crude shale oil is fractionated into gas, naphtha, gas oil, and bottoms oil. Subsequent hydrotreating and coking is used to upgrade the products to plant fuel gases and LPG, low sulfur fuel oil, diesel fuel, plus sulfur, ammonia, and petroleum coke byproducts.

TOSCO has presented considerable detail regarding proposed pollution control technologies to be utilized throughout its various operations (mining, retorting, upgrading). In the case of the retorting plant, a venturi wet scrubber is to be used for dust control in the shale preheat system, together with settling chambers and cyclones. Hot flue gases in the preheat system will be incinerated prior to discharge, in order to reduce trace hydrocarbons. Warm flue gas and a high energy venturi scrubber will remove residual dust from the ball recirculation system. A foul water stripper is planned to remove most of the NH_3, H_2S, and CO_2 gases from plant waters. Plant fuel gases will be treated to reduce the sulfur and nitrogen present, prior to on-site use for heat generation. TOSCO has indicated H_2S recovery as elemental sulfur in a Claus Plant, with tail gas treatment for trace SO_2 removal in a Wellman-Lord unit. Arsenic is removed from the gas oil and naphtha prior to hydrogenation by a proprietary catalytic process. Emissions from the moisturizing of spent shale are controlled by a venturi wet scrubber.

Process Use--

The TOSCO II technology is being considered for use by three shale oil developers: the TOSCO Corporation on their TOSCO Sand Wash Project, TOSCO and ARCO forming the Colony Development Company, and by Sohio Natural Resource Company at White River Shale project. The TOSCO Corporation has leases on five tracts of land totalling 5,949 ha (14,688 acres) at its Sand Wash Oil Shale property about 56 k (35 miles) south of Vernal, Utah. The company is in the second year of an eight year plan, under terms of a Unitization Agreement with the state of Utah, to prepare the leases for eventual commercial development. In December 1978, the Utah Conservation Committee and the State Division of Oil, Gas and Mining issued permits for TOSCO Corporation to sink an experimental mine shaft on the Sand Wash properties. The experimental mine shaft will have a diameter of 3.67 m (12 feet) and a depth of 732 m (2,400 feet). Initial field work is scheduled to begin in 1979 with the shaft estimated to be completed in 18 months to 3 years. An experimental mining program will follow when the shaft sinking is completed. During this experimental mining phase no on-site processing of the oil shale is planned, but shale samples will be sent to TOSCO's Research Center near Golden, Colorado for retorting in a .1 L/kg (25 TPD) TOSCO II pilot-plant. Information from the experimental mining program will be used to help prepare final design criteria for a commercial facility. TOSCO recently completed a preliminary design and updated cost estimate for eventually building a commercial-sized plant at Sand Wash. The proposed commercial plant would use the company's aboveground TOSCO II Process to extract petroleum liquids, gases and byproducts from crushed oil shale rock. Six 1.0 x 10^2 kg/day (11,000 ton/day) TOSCO II retort modules would be included, along with equipment for product storage and loading, utilities and disposal of spent shale [36]. Site exploration, environmental monitoring and shaft sinking is currently underway on the site.

In 1964 TOSCO with SOHIO and Cleveland Cliffs Iron Company formed the Colony Development Company to demonstrate the TOSCO II process on a semiworks scale. Ashland Oil and Shell Oil eventually replaced SOHIO and Cliffs. Atlantic Richfield joined the Colony group in 1969 when a second semiworks program was initiated [36]. In 1972, the Colony group (now composed of ARCO and TOSCO) completed operations on its 1,000 TPD TOSCO II semiworks plant on Parachute Creek, and prepared a design for a 50,000 barrel/day commercial plant [18]. A final EIS for the project was approved in 1977. Colony is now in the process of applying for the permits necessary to construct a commercial project on their Davis Gulch site, definite plans to proceed with plant construction have not yet been released [36].

Oil shale at the Davis Gulch site will be room-and-pillar mined and retorted using TOSCO II technology [36].

The White River Shale Project was formed in June 1974 by Phillips Petroleum Company and Sun Oil Company (now Sunoco Energy Development Company), the owners of the Federal Oil Shale Lease to U-a, and Sohio Petroleum Company (now Sohio Natural Resources Company), the owner of the Federal Oil Shale Lease to U-b, for the purpose of preparing and implementing a plan for the joint development of two lease tracts. Phillips and Sun were awarded the U-a lease in May 1974 for a bonus bid of approximately $75.6 million. The White River Shale Oil Corporation (Phillips, Sun and Sohio) was awarded the U-b lease for a bonus bid of approximately $45.1 million, but the tract has since been fully assigned to Sohio Natural Resources Company [36]. The project activities planned for the tracts are expected to occur in four phases. In Phase I a 335 meter (1,100 ft) deep access shaft for a subsequent room-and-pillar mine will first be established near the center of the combined tracts, in order to permit testing of the shale deposit. Mining will be initiated some six months later. Mine development will continue, and extend throughout the following Phase II, with an expansion of production from 1.81×10^6 kg (2,000 tons) to 9.10×10^6 kg (10,000 tons) of raw shale per day. Phase II will be of four years duration, and will involve the construction and operation of a single modular vertical retort with a throughput capacity of up to 9.10×10^6 kg of shale (10,000 tons) per day. The retort design has not yet been selected, but could be a Paraho direct-heat design later modified for indirect heating, or another available vertical-type retort. At a retort feed rate of 6.80×10^6 (7,500 tons) of coarse shale per day, some 750 cubic meters (4,700 barrels) of crude oil would be produced daily. A commercial plant (Phase III), with a first "train" projected capacity of 7.25×10^7 kg (80,000 tons) per day, will be constructed for start-up some 2 1/2 years after the successful conclusion of Phase II. This will be followed by start-up of a second commercial train of the same capacity some 1 1/2 years after the first, thus bringing total plant production capacity to an ultimate 1.45×10^8 kg (160,000 tons) per day. It is currently intended that the major portion (85%) of the Phases III and IV retorting will be carried out in vertical, gas-combustion type, direct and indirect-mode retorts, but that the 15% of crushing fines produced will be pyrolyzed in TOSCO II-type retorts. It is expected that all of the 15,800 cubic meters (100,000 barrels) of shale oil produced daily at maximum scale-up will be upgraded in facilities similar to those to be used for the Colony and Tract C-b projects. At present it is not known when, or on what basis, future development of tracts U-a and U-b will proceed. Lease terms were suspended in May 1977 until court resolution of land title [36].

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[36] Pollution Control Guidance for Oil Shale Development, by EPA Oil Shale Work Group, Revised draft report and appendices, July 1979.

Water Quality/Quantity Data--

A conceptual water flow diagram of a TOSCO II surface retort facility as designed by WPA is shown in Figure A-6. Water from retorting will be used in spent shale moistening after foul water stripping and organics removal.

Available water quality data is listed in Tables A-5 through A-7.

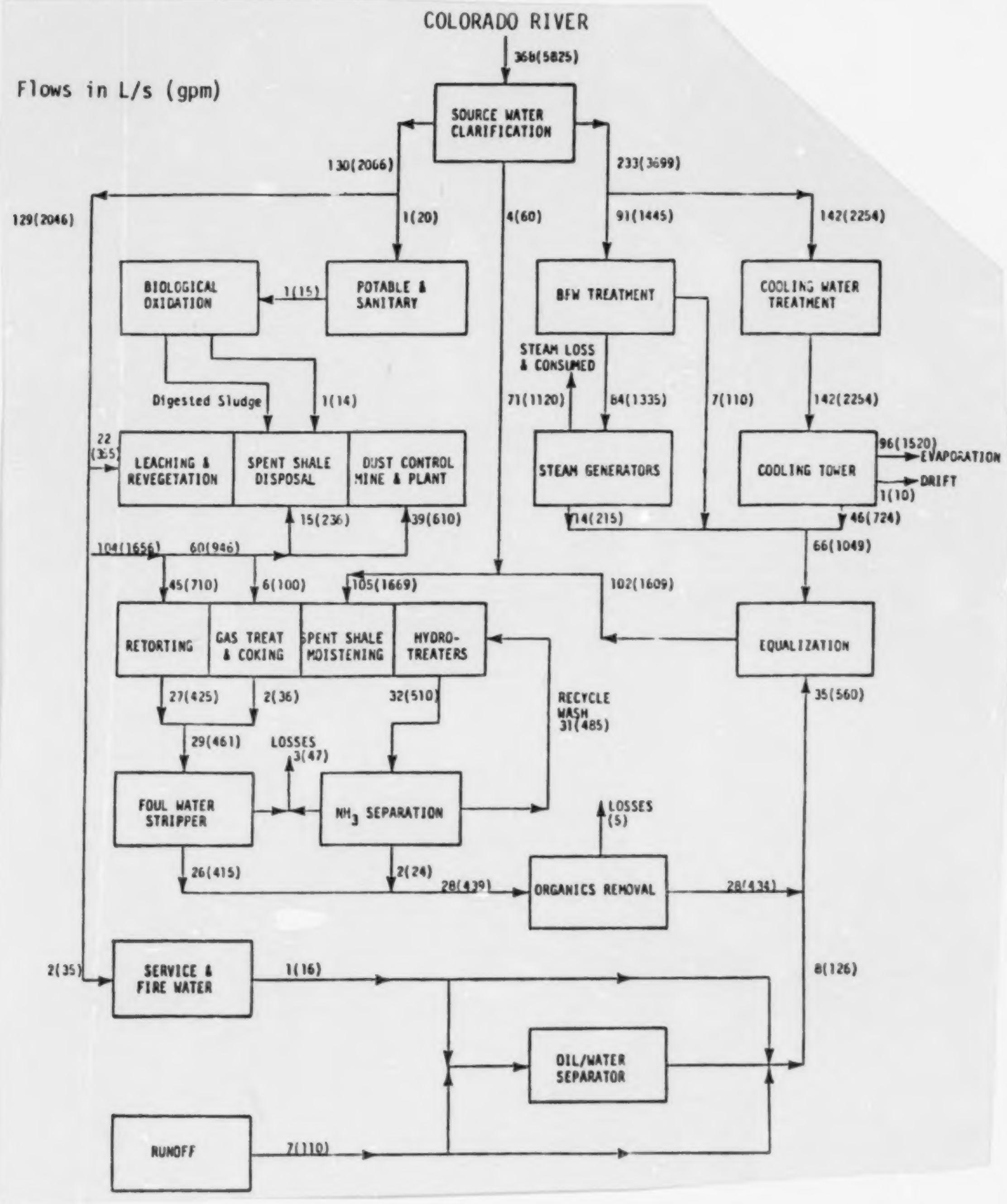
COLORADO RIVER
366(5825)
Flows in L/s (gpm)
SOURCE WATER CLARIFICATION
130(2066)
233(3699)
129(2046)
1(20)
4(60)
91(1445)
142(2254)
BIOLOGICAL OXIDATION
1(15)
POTABLE & SANITARY
BFW TREATMENT
COOLING WATER TREATMENT
STEAM LOSS & CONSUMED
Digested Sludge
1(14)
71(1120)
84(1335)
7(110)
142(2254)
22 (355)
LEACHING & REVEGETATION
SPENT SHALE DISPOSAL
DUST CONTROL MINE & PLANT
STEAM GENERATORS
COOLING TOWER
96(1520)
EVAPORATION
DRIFT
1(10)
15(236)
39(610)
14(215)
46(724)
104(1656)
60(946)
66(1049)
45(710)
6(100)
105(1669)
102(1609)
RETORTING
GAS TREAT & COKING
SPENT SHALE MOISTENING
HYDRO-TREATERS
EQUALIZATION
27(425)
2(36)
32(510)
RECYCLE WASH 31(485)
35(560)
29(461)
LOSSES 3(47)
FOUL WATER STRIPPER
NH3 SEPARATION
LOSSES (5)
26(415)
2(24)
28(439)
ORGANICS REMOVAL
28(434)
2(35)
SERVICE & FIRE WATER
1(16)
8(126)
OIL/WATER SEPARATOR
RUNOFF
7(110)

Figure A-6. Major water streams for TOSCO II process producing 7,500 m^3/day (47,000 BPSD) of upgraded shale oil, and 680 m^3/day (4,300 BPSD) LPG [27].

TABLE A-5. CHARACTERISTICS OF SOURCE WATERS - TOSCO PROCESS
mg/L

Species	Source water [28]	Source water[a] [34]	Clarified source water[b] [28]	Clarified source water[a,c] [34]	Cooling tower makeup[b,d] [28]	Boiler feed water[a,e] [34]
Alkalinity		150 - 250[b]		150 - 250[b]		<5
Ammonia		<1		<1		nil
COD						nil
Hardness		200 - 350[b]		200 - 350[b]		<5
Oil and grease		0 - 5		nil		nil
pH	7.4					
Phenols		<1		<1		nil
Phosphate (total)		0 - 1[f]		0 - 1[f]		nil
Silica	7.0					
TDS	734	400 - 800		400 - 800		50 - 100
Solids (suspended)		300 - 1,000		20 - 50		nil
Bicarbonate	168		124.3		24.9	
Calcium	72.0		179.3		179.3	
Chloride	205		289.0		289.0	
Magnesium	19.0		77.9		77.9	
Nitrate	8.6		7.0		7.0	
Potassium	5.3		6.8		6.8	
Sodium	145[d]		334.1		334.1	
Sulfate	158		177.8		290.1	

[a] Estimated data for White River Shale Project where Paraho technology will be used to retort rubblized shale, and TOSCO II technology will be used to retort fines.

[b] As $CaCO_3$.

[c] Following sedimentation and filtration.

[d] After neutralization of 80% of the alkalinity with H_2SO_4.

[e] Clarified source water following ion exchange and deaeration.

[f] mg/L PO_4.

TABLE A-6. CHARACTERISTICS OF WASTEWATERS - TOSCO PROCESS
mg/L

Species	Service water[a] [34]	Sanitary wastewater[a] [34]	Blowdowns[a,b] [34]	Condensed water from fractionation [37, 38]
Amines				994
BOD	50 - 500	20		14,075
Carboxylic acids				2,473
COD	100 - 2,000	50		26,550
Neutral oil				2,366
Oil and grease	50 - 1,000	<5		
pH				8.5
Solids (suspended)	30 - 500	30	100 - 500	
Silica				9
Phenols		<1		249
Specific conductance[c]				13,975
TDS	500 - 2,000	1,000 - 2,000	5,000 - 10,000	
TDS (organics removed)				7,470
TOC				17,425
Ammonia				3,353
Arsenic				0.08
Bicarbonate				10,820
Carbonate				2,273
Calcium				23.0
Chloride				1,101
Cyanide				<0.01
Fluoride				<1.0
Lithium				<10
Magnesium				6.4
Molybdenum				<1.0
Nitrate				288
Phosphate				4.2
Potassium				<5.0
Selenium				0.04
Sodium				<1.0
Sulfate				8
Sulfide				1,012
Sulfur (elemental)				<1.0
Sulfur (total)				1,020

[a] Estimated data for White River Shale Project where Paraho technology will be used to retort rubblized shale, and Tosco II technology will be used to retort fines.

[b] From cooling tower, steam generator and spent ion exchange reagent.

[c] In micro ohms per cm.

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[37] Metcalf & Eddy, Inc. Water Pollution Potential from Surface Disposal of Processed Oil Shale from the TOSCO II Process. Colony Development Operation, Denver, Colorado, October 1975.

[38] Water Management in Oil Shale Mining, Volume I. Prepared for U.S. Bureau of Mines under contract no. J0265019. Golder & Assoc., September 1977.

TABLE A-7. CHARACTERISTICS OF TREATED WASTEWATER AND SPENT SHALE LEACHATE - TOSCO PROCESS

mg/L

Species	Foul water stripper effluent[a,b] [34]	Expected foul water stripper effluent added to spent shale[c] [37, 39]	Treated stripper/ effluent/service water[a,d] [34]	Inorganic ion leachable from freshly retorted shales[e] [40]
Amines		410		
BOD			150 - 250	
COD	500 - 1,500			
Neutral oil		960		
Oil and grease	50 - 100		20 - 50	
Phenols	80 - 150	315	<1	
Solids (suspended)			200 - 300	
TDS			800 - 1,000	
Ammonia	25 - 50	16	10 - 15	
Arsenic		0.015 - 0.3		
Bicarbonate		100		
Calcium		280		3,150
Carbonate				
Chloride		570		3,080
Cyanide				
Magnesium		100		4,720
Phosphate		5	5 - 10	
Potassium				
Sodium		670		35,200
Sulfate		850		90,000
Zinc^{+2}		5		
Chromium^{+6}		2		

[a] Estimated data for White River Shale Project where Paraho technology will be used to retort rubblized shale, and TOSCO II technology will be used to retort fines.

[b] Stripper treating various gas and oil upgrading, and retort wastewater streams.

[c] In addition, elements present in trace quantities (less than 1 ppm) are Pb, Ce, Ag, Mo, Zr, Sr, Rb, Br, Se, Ci, Ni, Co, Fe, Mn, V, Ti, K, P, Al, F, B, and Li.

[d] Following flotation and biological oxidation.

[e] Maximum observed concentrations.

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[39] Colony, An Environmental Impact Analysis for a Shale Oil Complex at Parachute Creek, Colorado, Part 1: Plant Complex and Service Corridor, 1974.

[40] Synthetic Fuels Data Handbook, Cameron Engineers, Inc., T. A. Hendrickson. Denver, Colorado, 1975.

Superior Process

Process Description--

The Superior Oil Company has been working on a multimineral recovery (including the extraction of shale oil) process since 1967. Different from other potential shale oil extraction processes, Superior technology recovers rahcolite and dawsonite at the same time oil is extracted from oil shale.

Superior has developed commercial design configurations for both direct- and indirect-heated modes of operation of a circular grate retort adopted from commercially proven iron ore processing applications [41]. A simplified flow diagram for direct-heated oil shale retorting is provided in Figure A-7, and equipment sketches are provided in Figures A-8 and A-9.

A doughnut-shaped retort is divided into five separately enclosed sections: a loading zone, a heating zone, a residual carbon recovery zone, a cooling zone, and, to complete the circle, an unloading zone adjacent to the original loading sector [19]. Raw crushed shale enters through an airlock system, which together with circumferential water seals makes the unit gastight. The bed of shale loaded on the travelling grate passes first into the heating zone, where the shale is contacted by a stream of hot neutral or reducing gases that heat the shale to retorting temperature. The retorted shale travels from the retorting zone to the residual carbon recovery (or combustion) zone, where it is contacted with steam and air to form producer gas that provides fuel for the utility plant. Next, the retorted shale travels to the retort cooling zone where its temperature is reduced. It then moves to the unloading zone where it is discharged from the retort.

Upon leaving the heating zone of the retort, the stream of oil mist and process gas is contacted with water sprays [41]. The water spray serves to cool the gas and water vapor to saturation temperature, scrub out sulfur compounds, and stabilize the ionizing electrode and grounding plates in the electrostatic precipitator located downstream. Both wet and dry electrostatic precipitators were used to recover shale oil during testing of a 250 ton/day pilot plant [41].

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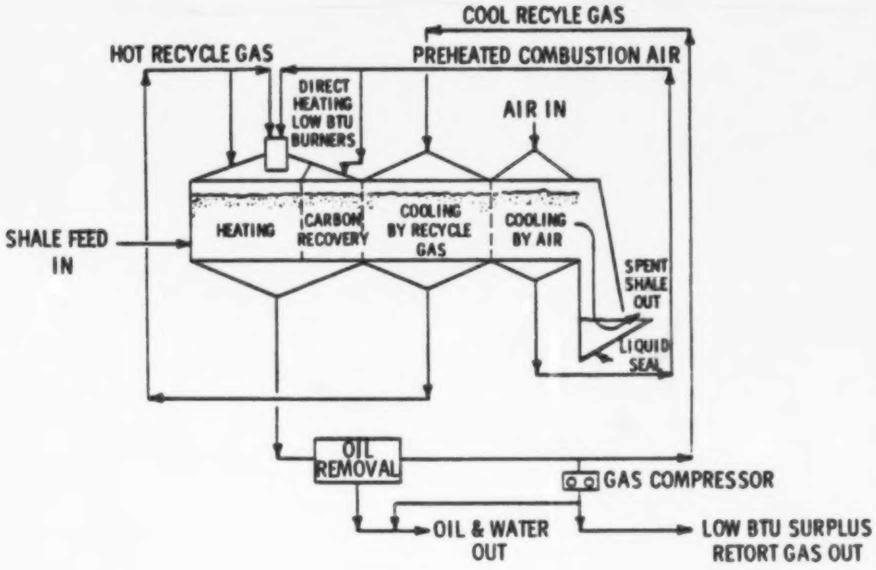
[41] Knight, J. H., and J. W. Fishback. Superior's Circular Grate Oil Shale Retorting Process and Australian Rundle Oil Shale Process Design. In: Twelfth Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, Colorado, August 1979. pp. 1-16.


COOL RECYLE GAS
HOT RECYCLE GAS
PREHEATED COMBUSTION AIR
DIRECT HEATING LOW BTU BURNERS
AIR IN
SHALE FEED IN
HEATING
CARBON RECOVERY
COOLING BY RECYCLE GAS
COOLING BY AIR
SPENT SHALE OUT
LIQUID SEAL
OIL REMOVAL
GAS COMPRESSOR
OIL & WATER OUT
LOW BTU SURPLUS RETORT GAS OUT

NOTE: THE CIRCULAR PATH OF THE SOLIDS BED IS PICTURED AS A STRAIGHT PATH FOR CLARITY

Figure A-7. Schematic diagram of Superior's commercial circular grate retort (direct-heated mode) [41].

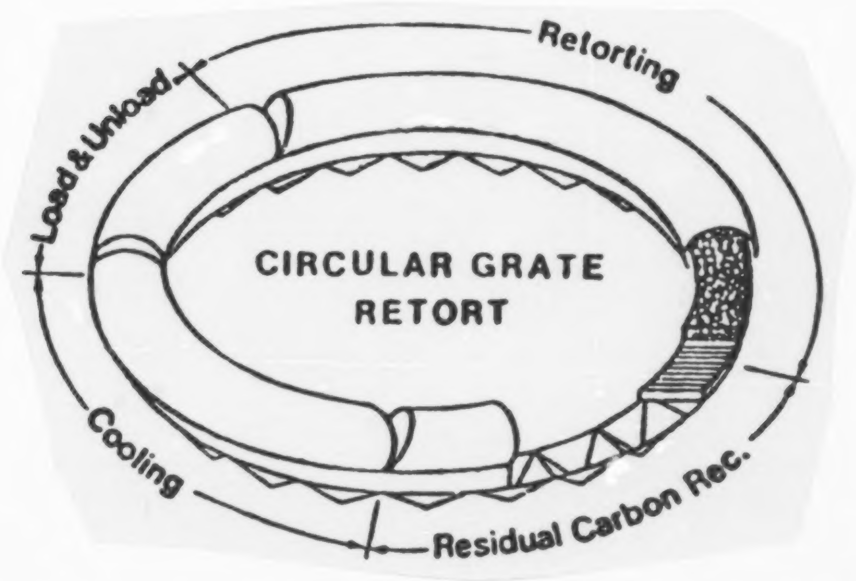

Retorting
Load & Unload
CIRCULAR GRATE RETORT
Cooling
Residual Carbon Rec.

Figure A-8. Functional Design of Superior retort [18].

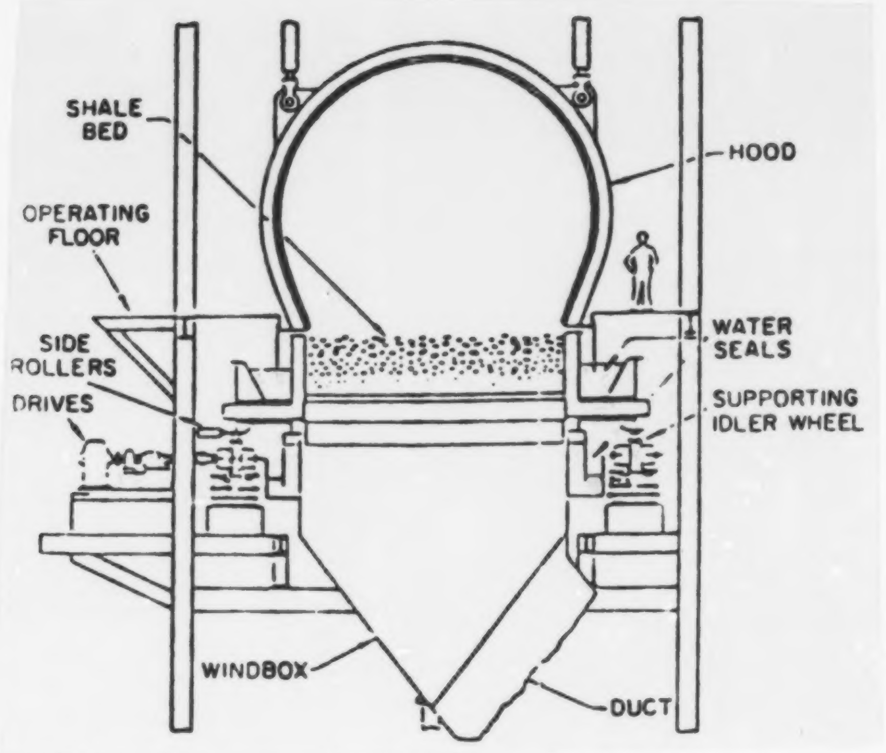


Figure A-9. Cross sectional view of Superior retort [18].

Process Use--

The Superior process has not been called for by any developer other than Superior Oil Company. Superior Oil Company has owned about 26 km^2 (6,500 acres) of land in the northern portion of Colorado's Piceance Creek basin for nearly 40 years [36]. In 1967, Superior initiated a research program for integrated recovery of oil shale and also saline minerals, dawsonite ($NaAl(OH)_2CO_3$), and nacolite ($NaHCO_3$), found at that site. However, in 1973, in order to block up a more manageable tract for commercial development using underground mining, Superior applied to the Bureau of Land Management of the Department of the Interior for a land exchange; a draft environmental impact statement regarding this action is currently under review [42]. Superior anticipates approval of the environmental impact statement by the end of this year, to be followed by a decision on the land exchange request by mid-1980; after that time, it will take three to five years to design, construct, and initiate operation of a commercial oil shale production facility (personal communication, J. William Fishback, Superior Oil Company, to Gerald M. Rinaldi, Monsanto Research Corporation, August 17, 1979).

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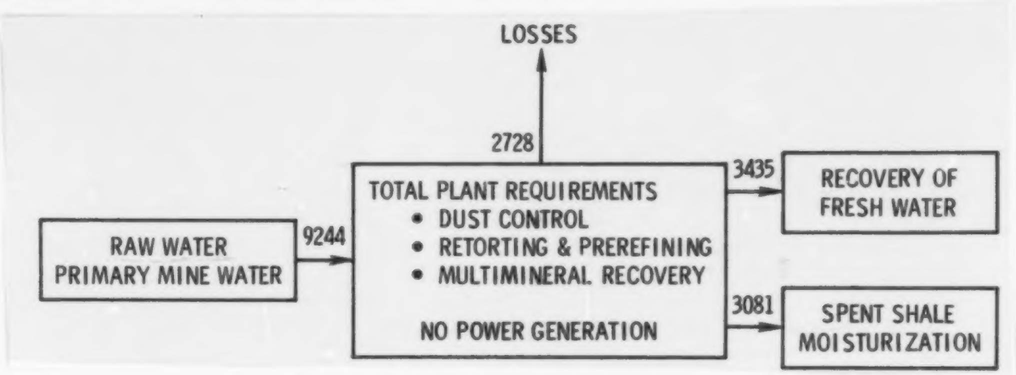
[42] Draft Environmental Statement: Proposed Superior Oil Company Land Exchange and Oil Shale Resource Development. U.S. Bureau of Land Management. Denver, Colorado. 1979. 105 pp.

Water Quality Data--
Water quality data from the Superior process is unavailable. It is expected that in addition to control of normal shale oil plant emissions and effluents, control of brines and wastes from the leaching plant and associated mineral recovery activities will be necessary [17]. In a second report [43], it is anticipated that fresh water will be recovered from the process, and the remainder will be used in spent shale moisturizing (see Figure A-10).


LOSSES
2728
TOTAL PLANT REQUIREMENTS
• DUST CONTROL
• RETORTING & PREREFINING
• MULTIMINERAL RECOVERY
NO POWER GENERATION
RAW WATER PRIMARY MINE WATER
9244
3435
RECOVERY OF FRESH WATER
3081
SPENT SHALE MOISTURIZATION

Multimineral Recovery
All flows in gallons per minute

Figure A-10. Overall water requirements for Superior's 100,000 BPD plant.

Union Process

Process Description [17]--

In the Retort B process, shown in Figure A-11, crushed oil shale in the size range of .32 to 5.0 cm flows through two feed chutes to a solids pump. The solids pump consists of two piston and cylinder assemblies which alternately feed shale to the retort; the pump is mounted on a movable carriage and is completely enclosed within the feeder housing and immersed in oil. As shale is moved upward through the retort by the upstroke of the piston, it is met by a stream of 510 to 540°C recycle gas from the recycle gas heater flowing downward. The rising oil shale bed is heated to retorting temperature by countercurrent contact with the hot recycle gas, resulting in the evolution of shale oil vapor and make gas. This mixture of shale oil vapor and make gas is forced downward by the recycle gas, and cooled by contact with the cold incoming shale in the lower section of the retort cone. In the disengaging section surrounding the lower cone, the liquid level is controlled by withdrawing the oil product, and the

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[43] An Analysis of Water Requirements for Oil Shale Processing by Surface Retorting, TID 27954.

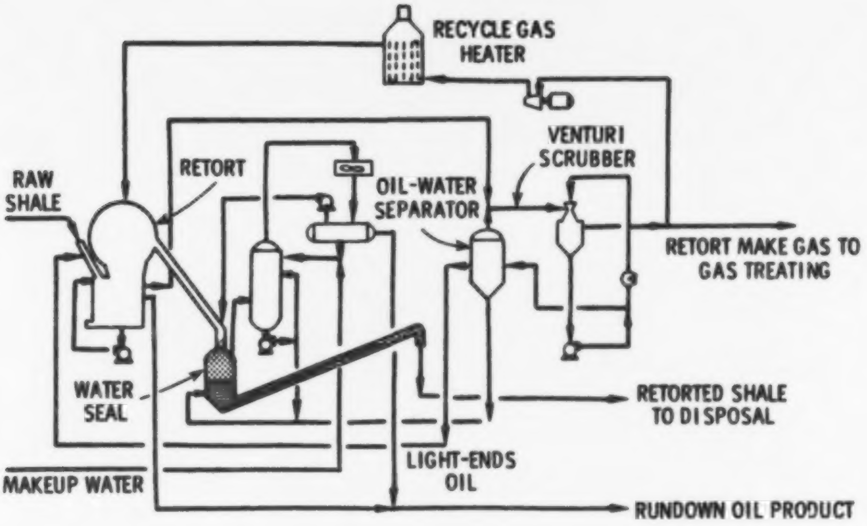
RECYCLE GAS HEATER
VENTURI SCRUBBER
RAW SHALE
RETORT
OIL-WATER SEPARATOR
RETORT MAKE GAS TO GAS TREATING
WATER SEAL
RETORTED SHALE TO DISPOSAL
LIGHT-ENDS OIL
MAKEUP WATER
RUNDOWN OIL PRODUCT

Figure A-11. Flow diagram for Union B retorting process [44].

recycle and make gas is removed from the space above the liquid level. As shown in Figure A-11, the make gas is first sent to a venturi scrubber for cooling and heavy ends removed by oil scrubbing. That portion of the 3.0 x 10^7 J/cm^3 (800 Btu/SCF) gas recycled is then processed by compression and oil scrubbing to remove additional naphtha and heavy ends, followed by hydrogen sulfide removal in a Stretford unit. The sweetened make gas is used as plant fuel.

The product oil withdrawn from the retort is treated sequentially for solids, arsenic, and light ends naphtha removal. The solids removal is accomplished by two stages of water washing. The shale fines are collected in the water phase which is recycled to the water seal. The water seal is a Union Oil concept shown in Figure A-11, in which a water level is maintained in a conveyor system for retorted shale removal to seal the retort pressure from atmosphere. For arsenic removal, a proprietary Union Oil process employing an adsorbent is utilized to reduce the arsenic content of the raw shale oil from 50 ppm to 2 ppm. The dearsenated shale oil is then sent to a stripping column for stabilization prior to shipment.

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[44] Hopkins, J. M., H. C. Huffman, A. Kelley, and J. R. Pawnall. Development of Union Oil Company Upflow Retorting Technology. Presented at the 81st AIChE National Meeting, April 11-14, 1976, Kansas City, Missouri.

For the Retort B process, all the plant fuel requirements will be met by the make gas produced. The principal pollution control devices in the Union Oil design include the Stretford process for hydrogen sulfide removal from the retort make gas and oil/water separation and sour water stripping for wastewater treatment. The treated wastewater is used in the cooling and moistening of retorted shale to provide for dust control and compaction.

Process Use--

Union Oil Company began development of its oil shale retorting technology in the early 1940s [45, 46]. The Union Retort A process was demonstrated at Brea, California, with 1,800-kg (2-ton)/day and 45,000-kg (50-ton)/day pilot-scale units. A 320-Mg (350-ton)/day semiworks was then operated near Grand Valley, Colorado, in the 1950s, achieving a throughput of 1,090-Mg (1,200-tons)/day when operations were suspended in 1958.

Two improved versions of this original process -- the Union Retort B process and the Steam Gas Recirculation (SGR) System -- were developed in the 1970s [36, 45, 46]. The Union Retort B process, although similar to A, uses external heating and recycling of the gaseous products. The Retort B process has been studied at the Union research facility but has not undergone large-scale testing. The SGR retorting system uses the "B" Retort to extract oil and gas from shale. The hot spent shale is then brought into contact with oxygen and steam, yielding low- or high-Btu fuel gas, depending on the nature of the oxygen source.

In 1978, Union announced plans for construction of a 9,070-Mg (10,000-ton)/day commercial module using the Retort B design at its Long Ridge site near the location of the earlier semiworks [36]. Union proposed a cooperative $120M venture to the DOE for development of such a commercial oil shale retorting facility. The prototype plant would be constructed on Union Oil property located on Parachute Creek, north of Grand Valley, Colorado.

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[45] Energy from the West: Energy Resource Development Systems Report, Volume III: Oil Shale. EPA-600/7-79-060c, U.S. Environmental Protection Agency, Washington, D.C. March 1979. 301 pp.

[46] Merrow, E. W. Constraints on the Commercialization of Oil Shale. R-2293-DOE, U.S. Department of Energy, Washington, D.C. September 1978. 133 pp.

Water Quality/Quantity Data--

Little has been published regarding the characterization of water streams other than boiler and cooling tower streams (see Table A-8) [36, 47]. It is apparent from Figure A-11, that the major end use of water in the Union B process is spent shale moisturizing as it is in many other surface retorting processes. Since gas condensates from the retort will be used ultimately for this purpose, it is expected that treatment of gas condensate similar to those required in the Paraho and Tosco II process will be necessary before the condensate can be mixed with the spent shale.

Lurgi-Ruhrgas Process

Process Description [36,17]--

Lurgi Company has been developing oil shale processing technology for the past 40 years. Two kilns were designed and installed for an Estonian Shale Oil Company in the late 1930's. Several other oil shale retorting processes were also developed by Lurgi to the commercial stage.

The Lurgi-Ruhrgas Process was developed in the 1950's for the low-temperature carbonization of subbituminous coal. It has also been used for olefin production using sand as the heat carrier. The process was demonstrated commercially in two units built in Yugoslavia in 1963. Tests on oil shale have been performed in equipment processing 16 TPD. American Lurgi has proposed scale-up to 8,000 TPD commercial-size retorts. Eight such plants can provide capacity for the production of 50,000 BPD shale oil.

The Lurgi-Ruhrgas process features the use of heat-carrier solids of small particle size, such as sand grains or spent shale solids derived from the retorting process. Figure A-12 is a simplified diagram of the process. The hot solids are mixed with finely crushed -0.6 cm (-1/4 inch) raw oil shale in a sealed screw-type conveyor. The organic constituents are pyrolyzed during the mixing which occurs in this device. Upon leaving the screw conveyor, the effluents are separated into solid and gaseous components in a collection bin. A portion of the spent solids is recycled to a lift pipe and the remainder is discarded. In the lift pipe, the hot spent shale is contacted with air at approximately 400°C (750°F), raising the material pneumatically, and simultaneously burning the carbon residue on the shale surface. The combustion gases and hot spent shale are separated at about 650°C (1,200°F) in a collecting bin and the solids are mixed again with incoming oil shale in the screw conveyor. Between six and eight pounds of heat-carrying solids are circulated and mixed with each pound of raw oil shale.

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[47] An Engineering Analysis Report on the Union B Process, TRW/ Denver Research Institute, EPA Contract 68-02-1881. March 1977.

TABLE A-8. CHARACTERISTICS OF VARIOUS WATER STREAMS IN THE UNION B PROCESS [36, 47]

	Ion exchange regeneration wastewater	Ion exchange backwash and rinse wastewater		Boiler feedwater
		Colorado River	White River	
TDS, mg/L	20,420	454	551	50
SS, mg/L	2,043	25	32	
Hardness, mg/L	9,889	214	300	5
Chloride, mg/L	2,780	119	42	15
Sulfate, mg/L	4,500	129	188	15
Calcium, mg/L	2,190	60	84	
Magnesium, mg/L	1,130	17	24	
Conductivity, μmhos/cm				75
Sodium, mg/L				10
Fluoride, mg/L				
Chromium, mg/L				

	Boiler blowdown	Cooling tower blowdown			
		Raw water supply source			
		Colorado River	White River	Upper Aquifer	Lower Aquifer
TDS, mg/L	331	1,589	1,929	3,360	32,900
SS, mg/L					
Hardness, mg/L	33	749	1,050	1,295	203
Chloride, mg/L	99	417	147	56	2,415
Sulfate, mg/L	99	452	658	1,120	280
Calcium, mg/L					
Magnesium, mg/L					
Conductivity, μmhos/cm	496	2,490	2,968	5,250	50,750
Sodium, mg/L	66	333	273	735	13,615
Fluoride, mg/L		-	1	4.9	98
Chromium, mg/L		53	53	53	53

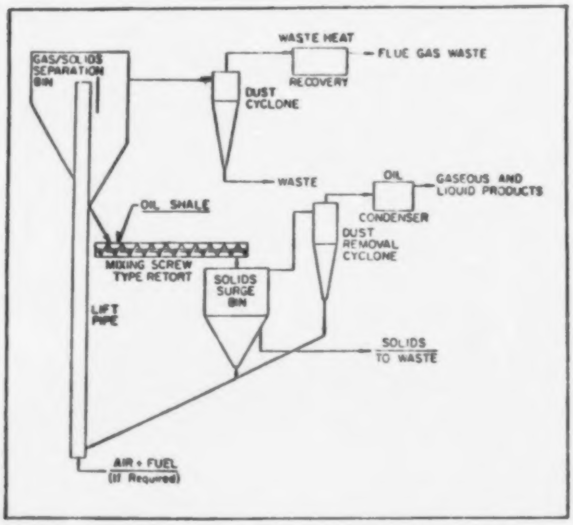
GAS/SOLIDS SEPARATION BIN
WASTE HEAT
RECOVERY
FLUE GAS WASTE
DUST CYCLONE
WASTE
OIL
GASEOUS AND LIQUID PRODUCTS
CONDENSER
DUST REMOVAL CYCLONE
OIL SHALE
MIXING SCREW TYPE RETORT
SOLIDS SURGE BIN
LIFT PIPE
SOLIDS TO WASTE
AIR + FUEL (If Required)

Figure A-12. Lurgi-Ruhrgas retorting process [20, 36].

Since no air is injected into the retorting area, the gas product from the process has a high heating value. Furthermore, the oil yield from the process typically ranges between 95% and 110% of Fischer Assay. Since the residual carbon on the spent shale is mostly utilized in the process, the overall thermal efficiency is quite high.

Process Use--

The Rio Blanco Oil Shale Company, comprised of Gulf Oil Corporation and Standard Oil Company (Indiana) presently intends to use two types of retorting technologies: the Lurgi-Ruhrgas process for above ground retorting, and the Rubblized *In-Situ* Extraction (RISE) process for below ground retorting [28]. Rio Blanco has leased tract C-a for oil shale retorting since March 1, 1974. In March, 1976, a Detailed Development Plan calling for open pit mining and surface retorting was submitted. Shortly thereafter, a one-year lease suspension was obtained because of a number of environmental and operational considerations. Rio Blanco submitted a revised DDP on May 25, 1977, which called for a ten-year Modular Development Phase to perfect modified *in-situ* retorting technology. This phase would be followed by a 30-year Commercial Development Phase at a planned capacity of 76,000 BPD [36].

Water Quality/Quantity Data--

The only data identified to characterize Lurgi-Ruhrgas wastewater is listed in Table A-9.

TABLE A-9. PROPERTIES OF LURGI-RUHRGAS GAS CONDENSATE WASTEWATER [36, 48]

Constituent	Concentration, mg/L
Total hydrocarbons (including phenols)	4,000
Dust	300
Ammonia	17,000
Sulfur	500
Phenols	260
pH	9.3

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[48] An Engineering Report on the Lurgi Retorting Process for Oil Shale. Prepared for the U.S. Environmental Protection Agency under Contract 68-02-1881, TRW. 1977.

MODIFIED *IN-SITU* PROCESSES

Occidental Process

Process Description [17, 18, 24]--
Occidental's modified *in-situ* process for shale oil recovery consists of retorting a rubblized column of broken shale, formed by expansion of the oil shale into a previously mined out void volume. The Occidental procces involves three basic steps. The first step is the mining out of approximately 20% of the oil shale deposits (preferably low grade shale or barren rock), either at the upper and/or lower level of the shale layer. This is followed by the drilling of vertical longholes from the mined-out room into the shale layer, loading those holes with an ammonium nitrate-fuel oil (ANFO) explosive, and detonating it with appropriate time delays so that the broken shale will fill both the volume of the room and the volume of the shale column before blasting. Finally, connections are made to both the top and bottom and retorting is carried out (Figure A-13).

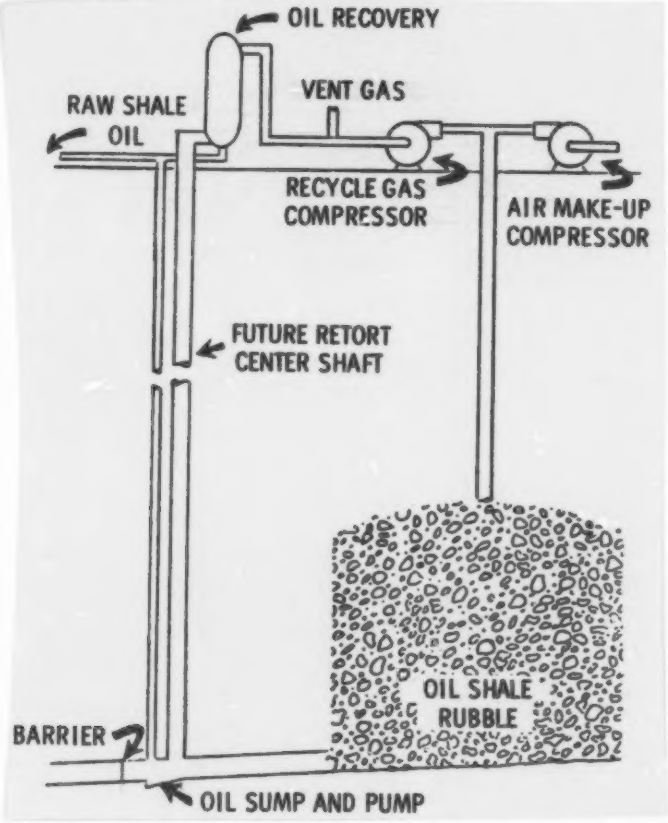
OIL RECOVERY
VENT GAS
RAW SHALE OIL
RECYCLE GAS COMPRESSOR
AIR MAKE-UP COMPRESSOR
FUTURE RETORT CENTER SHAFT
OIL SHALE RUBBLE
BARRIER
OIL SUMP AND PUMP

Figure A-13. Schematic of the Occidental modified *in-situ* process [17].

Retorting is initiated by heating the top of the rubblized shale column with the flame formed from compressed air and an external heat source, such as propane or natural gas. After several hours, the external heat source is turned off, and the compressed air flow (now mixed with steam) is maintained, utilizing the carbonaceous residue in the retorted shale as fuel to sustain combustion. In this vertical retorting process, the hot gases from the combustion zone move downwards to pyrolyze the kerogen in the shale below that zone, producing gases, water vapor, and shale oil mist which collects in the trenches at the bottom of the rubblized column (Figure A-14). The crude shale oil and byproduct water are collected in a sump and pumped to storage.

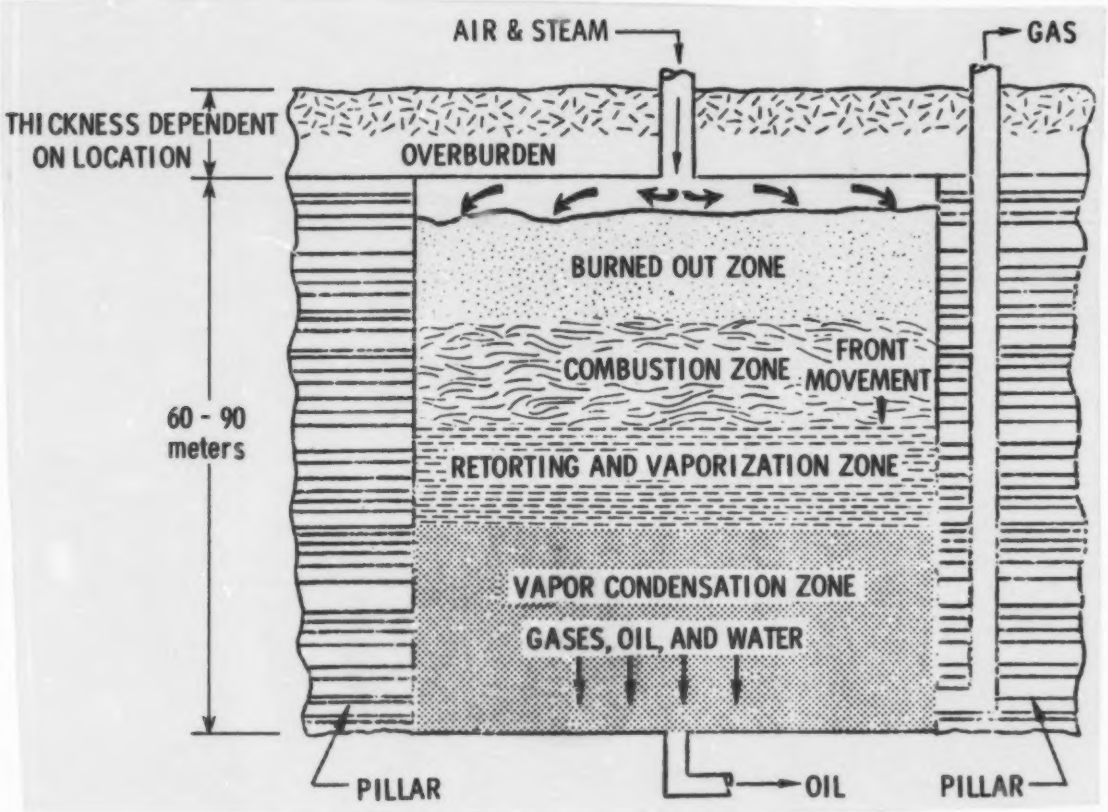
AIR & STEAM
GAS
THICKNESS DEPENDENT ON LOCATION
OVERBURDEN
BURNED OUT ZONE
COMBUSTION ZONE
FRONT MOVEMENT
60 - 90 meters
RETORTING AND VAPORIZATION ZONE
VAPOR CONDENSATION ZONE
GASES, OIL, AND WATER
PILLAR
OIL
PILLAR

Figure A-14. Flame front movement in the Occidental modified *in-situ* process [17].

The off-gas consists of products from shale pyrolysis, carbon dioxide and water vapor from the combustion of carbonaceous residue, and carbon dioxide from the decomposition of inorganic carbonates (primarily dolomite and calcite). Part of this off-gas is recirculated to control both the oxygen level in the incoming air and the retorting temperature. The off-gas has a heating value of approximately 2.4×10^6 J/cm^3 (65 Btu/SCF), and the part of the off-gas not recycled is currently flared.

Occidental envisions using the low Btu gas from a commercial retort for generating electric power. Turbines manufactured by Brown-Boveri of Switzerland will be investigated for this application. According to Occidental's estimate, only 20% to 25% of the electric power produced from the low-Btu gas is required for operating the modified *in-situ* process.

Occidental has not disclosed any information on the design of surface oil and gas treatment plants. The minimum treatment required for the crude shale oil produced from the retorting process will include phase separation of the oil from the by-product water and the stabilization of the oil product. The wastewater effluent from the phase separator may be used for steam generation after appropriate treatment.

Process Use--
The vertical, modified *in-situ* oil shale retorting process was conceived by Occidental Petroleum's in-house research firm, Garrett Research and Development Co., in the late 1960's [19, 49]. In May 1972, U.S. Patent 3,661, 423, "*In-Situ* Process for Recovery of Carbonaceous Materials from Subterranean Deposits," was assigned to Occidental Petroleum. Site development for field testing commenced in July 1972 at the head of Logan Wash, outside of DeBeque, Colorado. In the ensuing months, three research retorts were prepared and ignited. At the end of 1974, the project was transferred to Occidental Oil Shale, Inc., upon its establishment as a subsidiary of the Occidental Oil and Gas Production Division. The first commercial-size retort (No. 4), 76 m (250 ft) high with a cross section of 37 m (120 ft) square, was ignited in December 1975 and burned through June 1976 to produce 100 m^3 (27,500 gal) of crude shale oil [19]. As of February 1979, Retort No. 6, the third commercial-size operation, had produced nearly 5,090 m^3 (32,000 bbl), and a total of 11,900 m^3 (75,000 bbl) was expected to be produced before the burn was completed in April 1979 [50]. This ongoing development

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[49] Ashland Oil, Inc., and Occidental Oil Shale, Inc. Modifications to the Detailed Development Plan for Oil Shale Tract C-b. February 1977. 111 pp.

[50] Oxy's Logan Wash Retort No. 6 Burn Continues. Synthetic Fuels, 16(1):2-1 and 2-59, March 1979.

work is being conducted under a $60.5-M̄ cost-sharing DOE contract, signed in September 1977 [50].

In November 1976, Occidental Oil Shale formed a partnership with Ashland Oil for the development of Federal Prototype Oil Shale Lease Tract C-b in Rio Blanco County, Colorado [49]. Ashland withdrew in February 1979 [51], but in August, Tenneco Oil Company agreed to pay Occidental $110M̄ to acquire a 50% interest in Tract C-b [52]. One of the retort designs tested at Logan Wash will be used to construct 40 operating retorts that are capable of producing 9,060 m^3 (57,000 bbl) of shale oil daily by 1983, at the Tract C-b site [49].

Water Quality/Quantity Data--
A block flow diagram of the full-scale commercial facility at tract C-b, as envisioned by the developer, is shown in Figure A-15. Several water waste streams which appear in the diagram are:

- excess mine water
- blowdowns from water treatment and steam generation
- product water from oil/water separation.

In addition, the developer has noted that sanitary wastewater from several oil treatment units will exist.

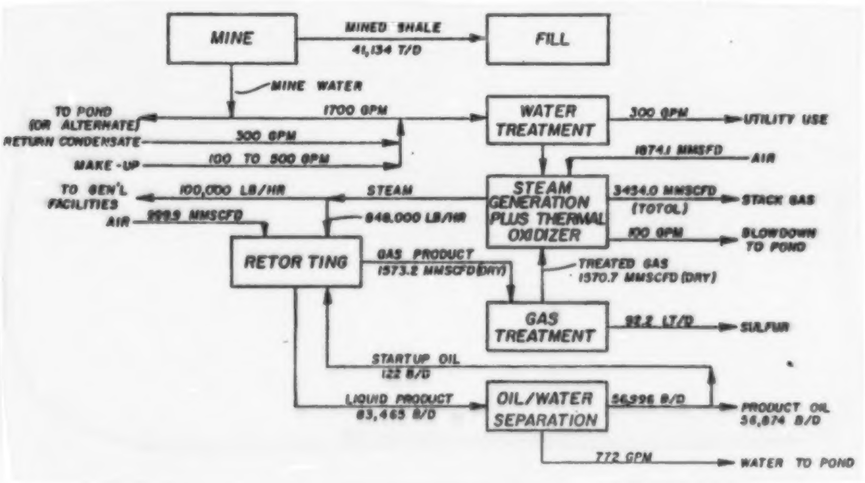
MINE
MINED SHALE
41,134 T/D
FILL
MINE WATER
TO POND (OR ALTERNATE)
1700 GPM
WATER TREATMENT
300 GPM
UTILITY USE
RETURN CONDENSATE
300 GPM
MAKE-UP
100 TO 500 GPM
1874.1 MMSFD
AIR
TO GEN'L FACILITIES
100,000 LB/HR
STEAM
STEAM GENERATION PLUS THERMAL OXIDIZER
3454.0 MMSCFD (TOTOL)
STACK GAS
AIR
999.9 MMSCFD
848,000 LB/HR
100 GPM
BLOWDOWN TO POND
RETOR TING
GAS PRODUCT
1573.2 MMSCFD (DRY)
TREATED GAS
1570.7 MMSCFD (DRY)
GAS TREATMENT
92.2 LT/D
SULFUR
STARTUP OIL
122 B/D
LIQUID PRODUCT
83,465 B/D
OIL/WATER SEPARATION
56,996 B/D
PRODUCT OIL
56,874 B/D
772 GPM
WATER TO POND

Figure A-15. Flow diagram of proposed commercial operation on tract C-b [49].

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[51] Ashland Withdraws from C-b Oil Shale Venture. Synthetic Fuels, 16(1):2-25, March 1979.

[52] News Flashes. Chemical Engineering, 86(17):89, August 13, 1979.

Occidental has characterized the aquifer water which would be characteristic of mine water as shown in Table A-10. Product water from an Occidental test retort at Logan Wash is also characterized in Table A-10.

Several options for disposal or reuse of waste waters are being considered by the developer [53]. For mine water, they include the following:

- disposal by evapotranspiration
- disposal by reinjection
- use as boiler feed after clarification, filtration, chemical addition for scale control, reverse osmosis, deionization and deaeration
- use as potable water or surface discharge after clarification, filtration, reverse osmosis, activated alumina, and chlorination
- use for dust control.

The developer is also considering several options for use of water treatment blowdowns and process wastewaters. These include:

- use for dust control
- moisturization of spent shale from surface retorting of shale removed from the modified *in-situ* retort
- ponding
- evaporating
- return to spent retort
- as a last resort, treatment for discharge.

Several of the above options have been included in a generalized water reuse scheme developed by WPA and DRI for a modified *in-situ* retorting facility such as Occidental's. This flow diagram is presented in Figure A-16.

Rubblized *In-Situ* Extraction (RISE) Process

Process Description--
The RISE process was conceived by the Lawrence Livermore Laboratory (at the University of California) in the early 1970's.

The RISE process is conceptually similar to Occidental's vertical, modified *in-situ* retorting process. About 20% of the oil shale

---

[53] Oil Shale Tract C-b. Detailed Development Plan and Related Materials, February 1976.

TABLE A-10. CHARACTERISTICS OF WASTEWATERS - OCCIDENTAL PROCESS
mg/L

	Mine dewatering [53]		Process water[a] [32, 54]
Constituent	Upper aquifer	Lower aquifer	
Bicarbonate	570	755	
Boron	1.5	3	18
Calcium	16	4	
Carbonate	0	11	9,780
Chloride	7	5	
Fluoride	18	19	34
Magnesium	10	3	
Sodium	300	310	3,540
Sulfate	4	12	1,270
TDS	560	750	9,690
pH (units)			8.5
Phenols			1.86
Potassium			93
Nitrate			1.8
TSS			33
Alkalinity as $CaCO_3$			10,650
Chromium			<0.1
Vanadium			<0.1
Nickel			<0.1
Copper			<0.1
TOC			1,020
Manganese			<0.1
Silver			<0.1
BOD_5			430
Oil and grease			150
Zinc			0.05
COD			3,490
Sulfite			10.5
Bromide			1.1
Kjeldahl N			1,420
Ammonia as N			1,200
Lithium			1.5
Arsenic			0.46
Iron			0.74
Molybdenum			0.23

[a] Average of four samples; process water from Retort 4 Logan Wash.

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[54] Loucks, R. A. Occidental Vertical Modified *In-Situ* Process for the Recovery of Oil from Oil Shale Phase I: Quarterly Progress Report for the Period May 1, 1978 through July 31, 1978, Occidental Oil Shale, Inc.

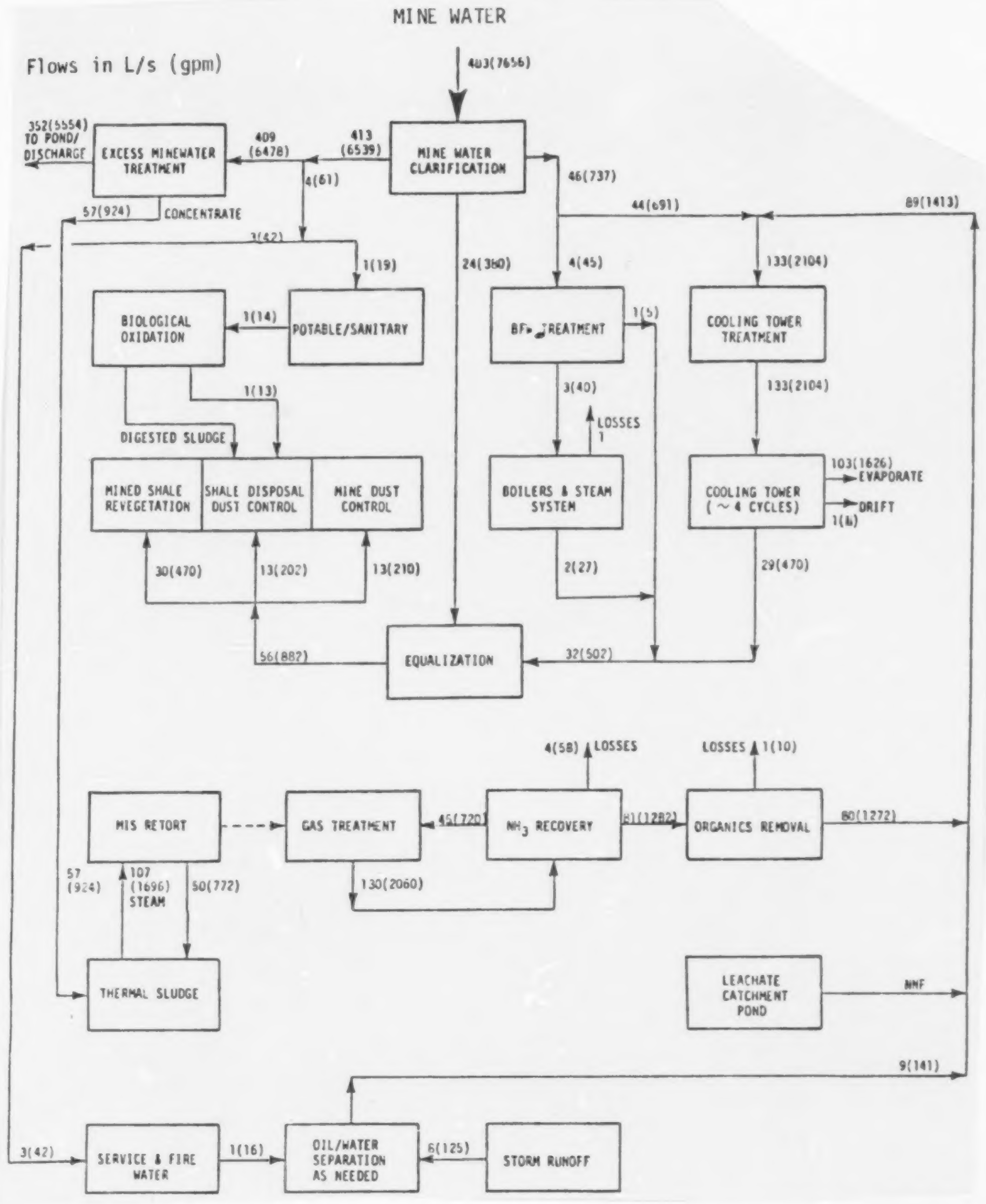
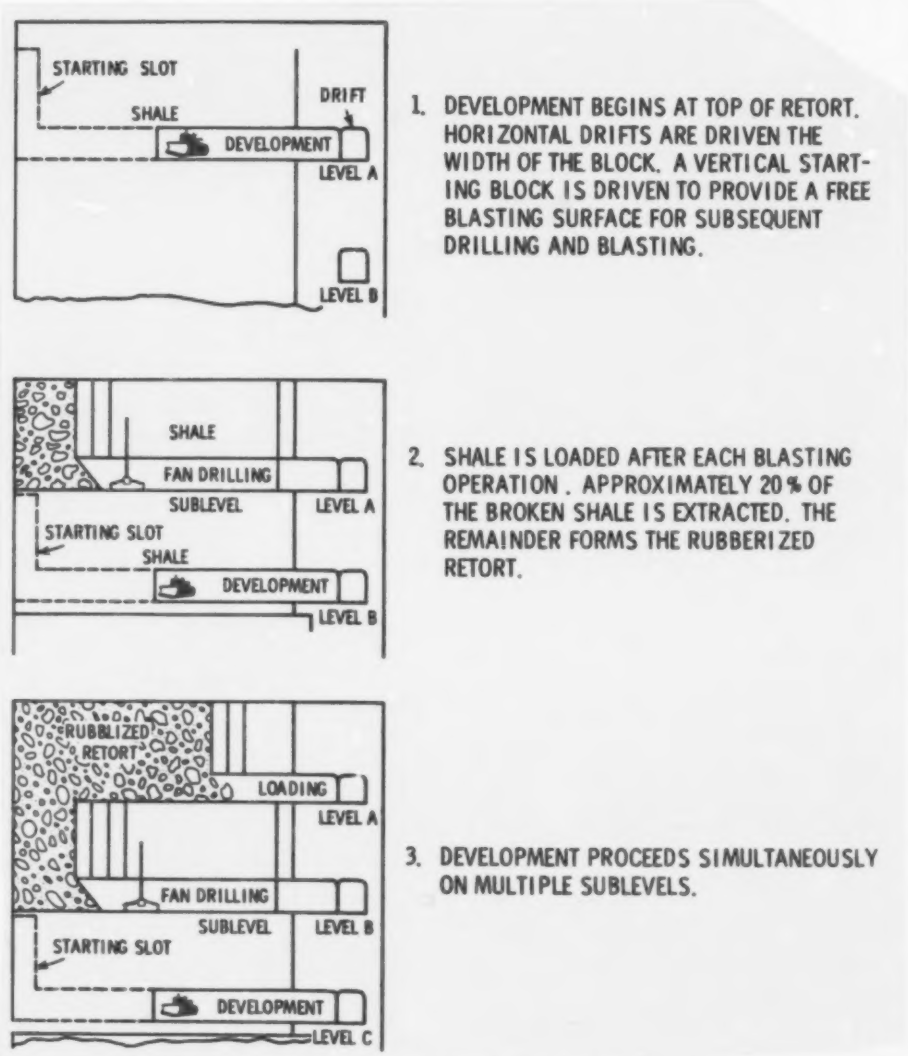

MINE WATER
Flows in L/s (gpm)
483(7656)
352(5554)
TO POND/
DISCHARGE
EXCESS MINEWATER TREATMENT
409
(6478)
413
(6539)
MINE WATER CLARIFICATION
4(61)
46(737)
57(924)
CONCENTRATE
44(691)
89(1413)
3(42)
1(19)
24(360)
4(45)
133(2104)
BIOLOGICAL OXIDATION
1(14)
POTABLE/SANITARY
BFW TREATMENT
1(5)
COOLING TOWER TREATMENT
1(13)
3(40)
133(2104)
LOSSES
1
DIGESTED SLUDGE
MINED SHALE REVEGETATION
SHALE DISPOSAL DUST CONTROL
MINE DUST CONTROL
BOILERS & STEAM SYSTEM
COOLING TOWER
(~ 4 CYCLES)
103(1626)
EVAPORATE
DRIFT
1(6)
30(470)
13(202)
13(210)
2(27)
29(470)
56(882)
EQUALIZATION
32(502)
4(58)
LOSSES
LOSSES
1(10)
MIS RETORT
GAS TREATMENT
45(720)
NH_3 RECOVERY
81(1282)
ORGANICS REMOVAL
80(1272)
57
(924)
107
(1696)
STEAM
50(772)
130(2060)
THERMAL SLUDGE
LEACHATE CATCHMENT POND
NNF
9(141)
3(42)
SERVICE & FIRE WATER
1(16)
OIL/WATER SEPARATION AS NEEDED
6(125)
STORM RUNOFF

Figure A-16. Major water streams for modified *in-situ* shale oil plant producing 9,000 m^3/day (57,000 bbl/day) crude shale oil [27].

will be continuously mined out using a modified sublevel caving technique described in Figure A-17 [45, 55]. The RISE process supposedly prepares more uniformly sized rubble than Occidental's technology [45], thus promoting better gas distribution [20].


STARTING SLOT
SHALE
DRIFT
DEVELOPMENT
LEVEL A
LEVEL B
SHALE
FAN DRILLING
SUBLEVEL
LEVEL A
STARTING SLOT
SHALE
DEVELOPMENT
LEVEL B
RUBBLIZED RETORT
LOADING
LEVEL A
FAN DRILLING
SUBLEVEL
LEVEL B
STARTING SLOT
DEVELOPMENT
LEVEL C

1. DEVELOPMENT BEGINS AT TOP OF RETORT. HORIZONTAL DRIFTS ARE DRIVEN THE WIDTH OF THE BLOCK. A VERTICAL STARTING BLOCK IS DRIVEN TO PROVIDE A FREE BLASTING SURFACE FOR SUBSEQUENT DRILLING AND BLASTING.
2. SHALE IS LOADED AFTER EACH BLASTING OPERATION. APPROXIMATELY 20% OF THE BROKEN SHALE IS EXTRACTED. THE REMAINDER FORMS THE RUBBERIZED RETORT.
3. DEVELOPMENT PROCEEDS SIMULTANEOUSLY ON MULTIPLE SUBLEVELS.

Figure A-17. Modified sublevel caving mining technique proposed for use in the RISE process [45, 55].

---

[55] Lewis, A. E., and A. J. Rothman. Rubble *In-Situ* Extraction (RISE): A Proposed Program for Recovery of Oil from Oil Shale. UCRL-51768. U.S. Energy Research and Development Administration Contract No. W-7405-Eng-48. March 1975. 26 pp.

The rubblized column, 46 m (150 ft) wide, 91 m (300 ft) long, and 229 m (750 ft) high on a commercial scale [56], is retorted by using hot gas to heat the oil shale [45]. This gas can be generated by combusting a portion of the oil shale with air, or it could be heated by external combustion [55]. The products from the underground retorts would be treated to remove entrained solids, and the oil would be fractionated into naphtha and a heavy oil stream for blending with the liquid products from surface retorting [36]. Product gas from the *in-situ* retorts, after removal of sulfur compounds, would be fed to gas turbines to generate electricity [36].

Process Use--
The RISE process will be used by the Rio Blanco Oil Shale Company on tract C-a for below ground retorting, while Lurgi-Ruhrgas retorting will be used above ground. The history of the Rio Blanco Oil Shale Company is presented earlier in this appendix on page 69.

Water Quality/Quantity Data--
As with the Occidental modified *in-situ* process, a block flow diagram of the commercial facility at tract C-a has been provided by the developer in Detailed Development Plans, and is shown in Figure A-18. Rio Blanco intends to discharge only excess water by aquifer reinjection while reusing the remaining mine water and retort water.

Analysis of retort wastewater is unavailable, however, groundwater analysis characteristic of mine dewatering water are provided in Table A-11.

DRI and WPA have analyzed the tract C-a processes and have prepared a water reuse scheme utilizing wastewaters from the MIS retort, Lurgi-Ruhrgas retort, and mine water. This scheme is presented in Figure A-19.

TRUE *IN-SITU* PROCESSES

Equity Process

Process Description--
Equity's BX process is unique in that superheated steam, at 540°C (1,000°F) and 10 MPa (1,500 psig), is used as a heat-carrying medium to retort leached-zone oil shale, and to provide a

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[56] Gulf Oil Corporation and Standard Oil Company (Indiana). Revised Detailed Development Plan for Oil Shale Tract C-a, three volumes. Denver, Colorado. May 1977.

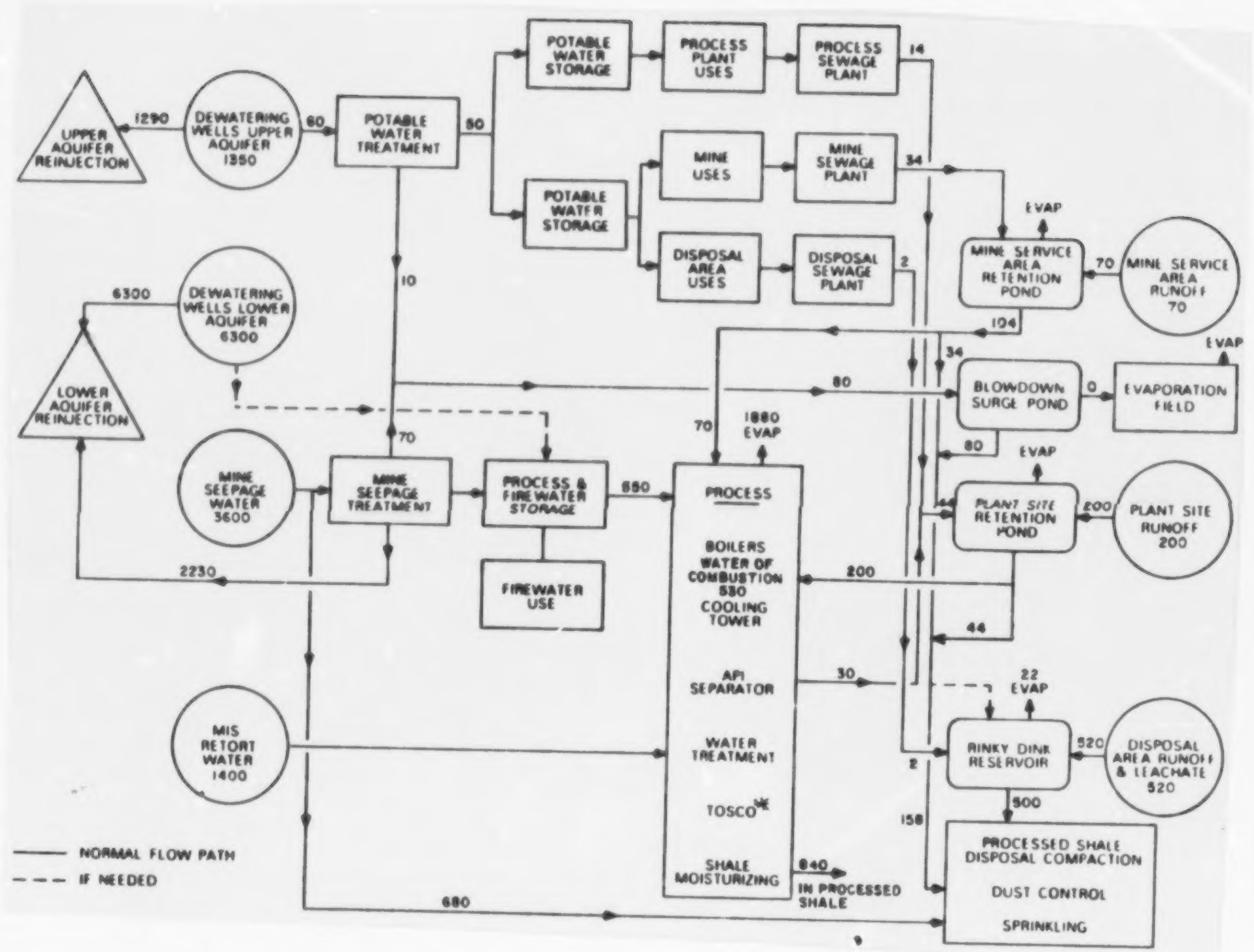
UPPER AQUIFER REINJECTION
1290
DEWATERING WELLS UPPER AQUIFER 1350
60
POTABLE WATER TREATMENT
50
POTABLE WATER STORAGE
PROCESS PLANT USES
PROCESS SEWAGE PLANT
14
POTABLE WATER STORAGE
MINE USES
MINE SEWAGE PLANT
34
DISPOSAL AREA USES
DISPOSAL SEWAGE PLANT
2
EVAP
MINE SERVICE AREA RETENTION POND
70
MINE SERVICE AREA RUNOFF 70
10
6300
DEWATERING WELLS LOWER AQUIFER 6300
LOWER AQUIFER REINJECTION
104
34
80
BLOWDOWN SURGE POND
0
EVAPORATION FIELD
EVAP
70
1880 EVAP
70
80
EVAP
MINE SEEPAGE WATER 3600
MINE SEEPAGE TREATMENT
PROCESS & FIREWATER STORAGE
650
PROCESS
BOILERS WATER OF COMBUSTION 530 COOLING TOWER
44
PLANT SITE RETENTION POND
200
PLANT SITE RUNOFF 200
2230
FIREWATER USE
200
44
API SEPARATOR
30
22 EVAP
MIS RETORT WATER 1400
WATER TREATMENT
RINKY DINK RESERVOIR
520
DISPOSAL AREA RUNOFF & LEACHATE 520
2
TOSCO*
500
158
PROCESSED SHALE DISPOSAL COMPACTION
DUST CONTROL
SPRINKLING
SHALE MOISTURIZING
840
IN PROCESSED SHALE
680
NORMAL FLOW PATH
IF NEEDED

Figure A-18. Water flow - commercial phase - GPM [57].

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[57] Detailed Development Plan, Vols, I-V, Federal Oil Shale Lease Tract C-a (Rio Blanco Oil Shale Project), submitted to Area Oil Shale Supervisor. March 1976.

TABLE A-11. CHARACTERISTICS OF WASTEWATER - RISE PROCESS
mg/L

	Mine dewatering [17, 57]	
Parameter	Upper aquifer	Lower aquifer
TDS	1,140	1,500
Boron	0.692	1.830
Copper	0.027	0.018
Cyanide	0	0.005
Arsenic	0.004	0.001
Barium	0	0
Cadmium	0.002	0.001
Chromium	0.005	0
Lead	0.353	0.647
Mercury	0	0
Nitrate as N	0.534	0.765
Selenium	0	0
Silver	0.007	0.003
Fluoride	4.090	13.700

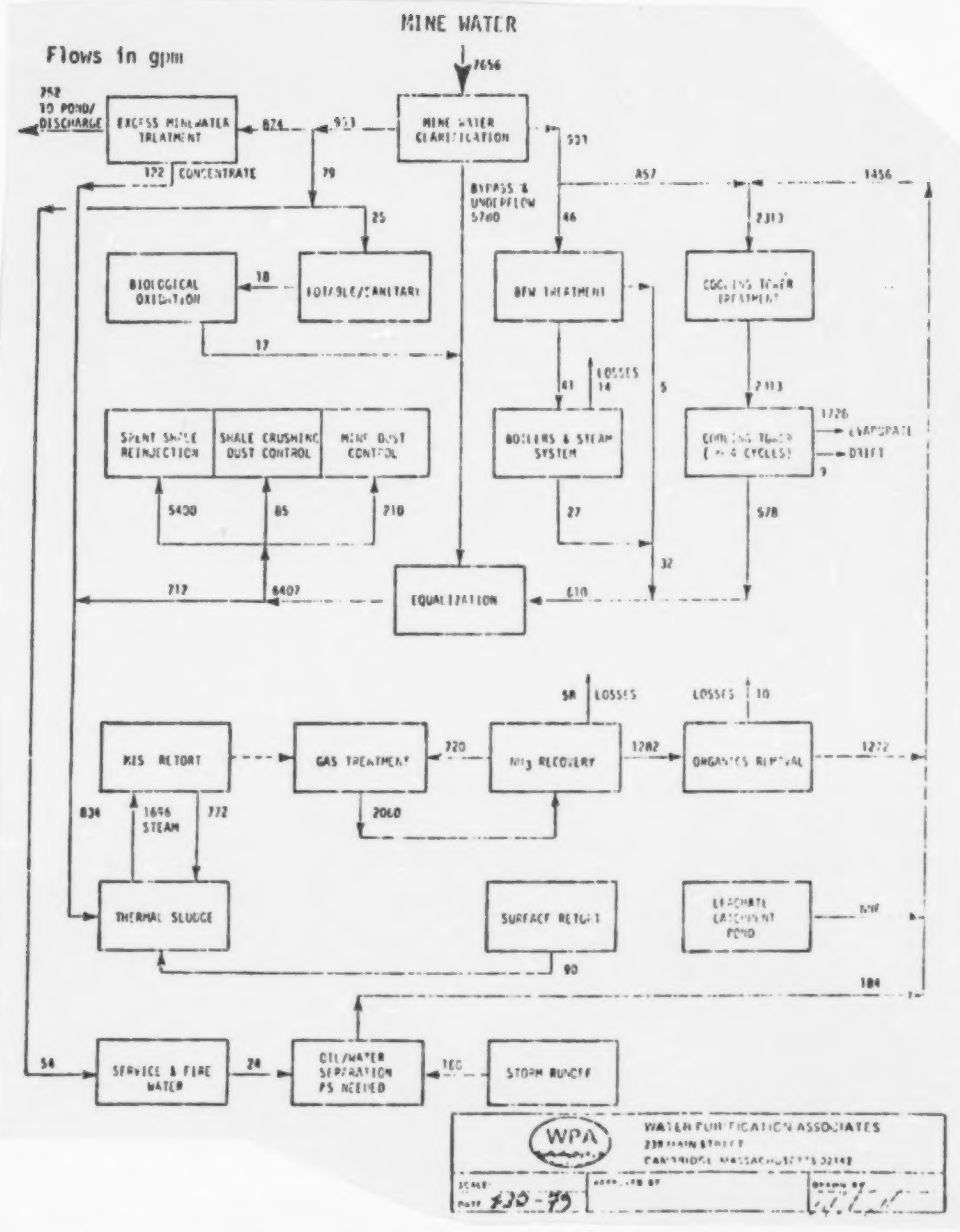
MINE WATER
Flows in gpm
7656
752
TO POND/ DISCHARGE
EXCESS MINEWATER TREATMENT
824
953
MINE WATER CLARIFICATION
931
172
CONCENTRATE
79
BYPASS & UNDERFLOW 5700
857
1456
25
46
2313
BIOLOGICAL OXIDATION
18
POTABLE/SANITARY
BFW TREATMENT
COOLING TOWER TREATMENT
17
41
LOSSES 14
5
2113
1726
EVAPORATE
DRIFT
9
SPENT SHALE REINJECTION
SHALE CRUSHING DUST CONTROL
MINE DUST CONTROL
BOILERS & STEAM SYSTEM
COOLING TOWER (4 CYCLES)
5400
85
210
27
578
32
712
6407
EQUALIZATION
610
58
LOSSES
LOSSES
10
MIS RETORT
GAS TREATMENT
720
NH3 RECOVERY
1282
ORGANICS REMOVAL
1272
834
1696 STEAM
772
2060
THERMAL SLUDGE
SURFACE RETORT
LEACHATE CATCHMENT POND
90
184
54
SERVICE & FIRE WATER
24
OIL/WATER SEPARATION AS NEEDED
100
STORM RUNOFF
WPA
WATER PURIFICATION ASSOCIATES
238 MAIN STREET
CAMBRIDGE, MASSACHUSETTS 02142
SCALE:
DATE 4-30-79
APPROVED BY
DRAWN BY

Figure A-19. Major water streams for modified *in-situ* Lurgi-Ruhrgas shale oil plant producing 81,000 bbl/day crude shale oil. Minewater rate of 7,656 gpm from MIS scheme with no surface retorting [27].

mechanism for the recovery of the shale oil [58]. The leached zone is a geological formation in which the shale content has been upgraded by natural dissolution of inorganic saline minerals to produce higher porosity and permeability. The oil shale will be retorted by injecting steam into the leachate zone and recovering steam, water, oil, and gas through an array of production wells.

A sophisticated steam generating plant, a water treatment plant, water storage facilities, and an instrumentation system are needed to facilitate injection of 6.0×10^{10} J (5.7×10^7 Btu) of steam per hour [58]. Figure A-20 is a flow diagram depicting the basic elements of the Equity oil shale retorting process [58].

Water produced from the leached zone is held in the water storage pit until it can be processed in the two water treatment plants. After treatment, the water is stored in five 64-m^3 (400-bbl) tanks. As needed, treated water is fed to two steam generators capable of producing dry steam at 320°C (605°F) and 11 MPa (1,600 psig), after which the steam is superheated to 540°C at 10 MPa (1,500 psig) [58]. From the superheater, the steam is distributed to eight injection wells; the quantity sent to each well is proportionately controlled by automatic valves. The steam is injected through insulated 70-mm (2 3/8-in.) steel tubing suspended in a 180-mm (7-in.) steel casing that is perforated at the top and bottom of the leached zone [59].

Condensed steam and retorted oil and gas are withdrawn from the middle of the leached zone by five production wells. On the surface, oil, gas, and water from the production wells are separated. Water is returned to the water storage pit, and product gas is recovered for use as fuel for the steam generators.

Process Use--

Equity Oil Company, under the Department of Energy's Cooperative Agreement No. ET-78-F-03-1747, is conducting a demonstration of *in-situ* oil shale retorting technology. The test location for the so-called BX *In-Situ* Oil Shale Project is Section 6, Township 3 South, Range 98 West, near the center of the Piceance Creek basin in Colorado [58]. At this site the leached zone is 165 m (540 ft) thick, the oil content of the shale averages about 100 $m^3/10^6$ kg (24 gal/ton), and the overburden thickness is about 240 m (800 ft) [58]. The planned period of operation for

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[58] Equity/DOE BX *In-Situ* Project is Progressing. Synthetic Fuels, 16(1):pp. 2-6 through 2-9, March 1979.

[59] CPI News Briefs. Chemical Engineering, 86(17):102, August 13, 1979.

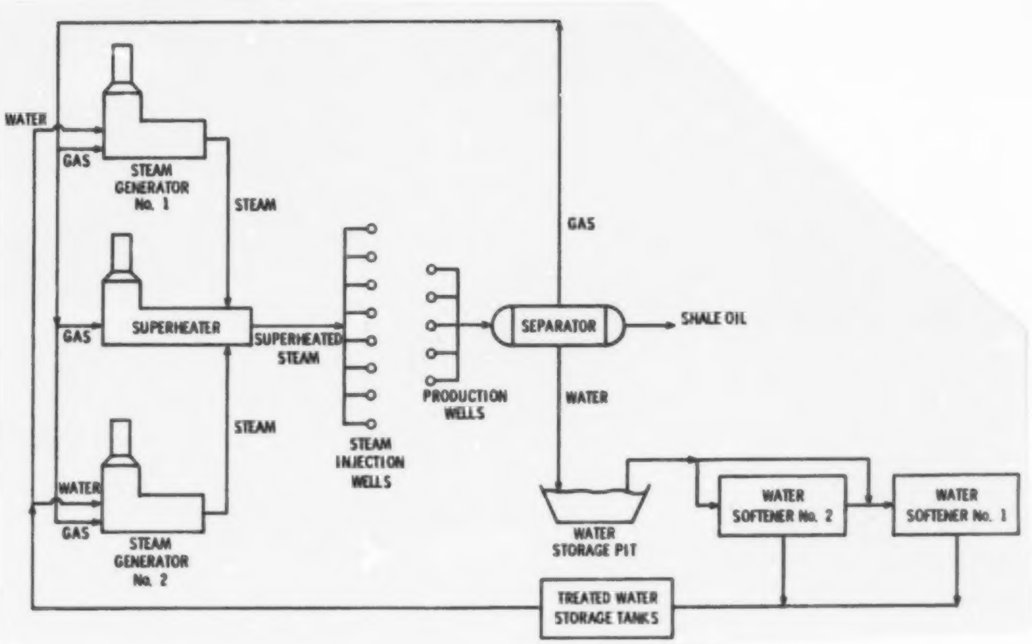
WATER
GAS
STEAM GENERATOR No. 1
STEAM
GAS
SUPERHEATER
SUPERHEATED STEAM
STEAM
WATER
GAS
STEAM GENERATOR No. 2
STEAM INJECTION WELLS
PRODUCTION WELLS
GAS
SEPARATOR
SHALE OIL
WATER
WATER STORAGE PIT
WATER SOFTENER No. 2
WATER SOFTENER No. 1
TREATED WATER STORAGE TANKS

Figure A-20. Flow diagram for Equity's BX *In-Situ* Oil Shale Project [58].

Equity's BX project is approximately two years, during which time 1.1 x 10^{15} J (1.0 x 10^{12} Btu) of superheated steam will be injected into the leached zone, and at least 79,500 m^3 (500,000 bbl) of oil will be recovered [58]. The $6.5-M̄ cost of the 55-month project is to be shared by Equity (14%), and by DOE (86%) [58, 60].

Water Quality/Quantity Data--
Process wastewater from the Equity process is produced along with the shale oil pumped from the retort and as a vapor carried with the off-gases. Process wastewater will consist of water present in the formation, condensed injected steam, and moisture produced from chemical reactions of the retorting process. No information is presently available on the quantity or quality of this wastewater; however, it has been suggested that Equity process wastewater is similar to that from the Paraho process operating in the indirect mode. In addition, it has been suggested that the retort groundwater may be similar to alluvial water analyzed at the Equity site. Based on these assumptions, composition of Equity process water has been estimated and is shown in Table A-12 [32].

---

[60] Equity Oil/ERDA Sign Cooperative Agreement. Synthetic Fuels, 14(3):2-31, September 1977.

TABLE A-12. SUMMARY OF EQUITY PROCESS WASTEWATER COMPONENT CONCENTRATIONS[a] [32]

Parameter	Groundwater	Retort water[b]	Synthesis wastewater[c]
Calcium, mg/L	94.9	37.9	6.6
Magnesium, mg/L	43.1	540	29
Sodium, mg/L	65.3	278	17
Potassium, mg/L	1.63	25.3	1.3
Carbonate (as CO_3), mg/L	0	28,890	1,400
Bicarbonate, mg/L	463	-	50
Sulfate, mg/L	57.1	9,140	460
Chloride, mg/L	1.06	1,740	90
Nitrate (as N), mg/L	1.73	-	0.2
Fluoride, mg/L	0.39	1.96	0.12
Boron, mg/L	0.29	35.0	1.8
Silica, mg/L	0.35	32.0	1.6
Ammonium, mg/L	-	-	-
TOC, mg/L	10.8	32,800	1,600
COD, mg/L	19.5	75,720	3,800
TKN, mg/L	5.77	18,000 assumed	900
NH_3 (as N), mg/L	0.24	32,520	1,600
pH, units	7.65	8.34	8.05
Conductance, $\mu\Omega$/cm	1,180	-	-
Hardness (as $CaCO_3$), mg/L	417	2,320	140
TDS, mg/L	790	30,000 assumed	1,500
Alkalinity (as $CaCO_3$), mg/L	380	24,700	1,300
Total chromium, mg/L	<0.1	0.11	0.01
Selenium, mg/L	<0.01	12.5	0.63
Mercury, mg/L	<0.01	13.5	0.68
Arsenic, mg/L	<0.1	9.0	0.46
Iron, mg/L	0.05	6.45	0.33
Suspended solids, mg/L	1,970	84	100
Sulfide, mg/L	-	0	-
Oil and grease, mg/L	16.9	-	-
Cadmium, mg/L	<0.1	0.22	0.02
Lead, mg/L	<0.1	2.25	0.12
Molybdenum, mg/L	<0.1	1.85	0.10
Cyanide, mg/L	<0.1	5.20	0.27
Phenol, mg/L	-	4.06	0.20

[a] Average of analyses of several alluvial well samples reported by Equity. Represents best groundwater quality data available.

[b] Results of Paraho - Semiworks retort water quality analyses. Represents best data available from a noncombustion retort on similar shales.

[c] Weighted average of groundwater, retort water and condensed steam at the ratios of 5:5:90, respectively. Condensate parameter concentrations all assumed 0.

Dow Processes

Process Descriptions--

Dow Chemical Co. is currently considering three main operational strategies for retorting Michigan Antrim oil shale [61]. Separated Front Pyrolysis/Combustion (SFPC) represents conventional *in-situ* oil shale extraction technology [62]. However, this may not be the optimum strategy because Antrim shale produces less gas and oil and more char during pyrolysis than do the western shales. Therefore, more of the potentially recoverable energy would remain in the shale after pyrolysis.

The second operation strategy being considered by Dow is gasification [61]. The gas and oil products of pyrolysis would be burned *in-situ* to generate a hot char bed, which would be gasified with air and steam.

Combined Pyrolysis/Combustion/Gasification (CPCG) is the third operational strategy considered by Dow [61]. CPCG seeks to increase the efficiency of energy extraction by employing both SFPC and gasification. Limited data supporting the possible success of this strategy have been obtained in horizontal, modified *in-situ* trials. A strategy such as this would allow Dow to take advantage of the tendency of Antrim shale to produce char while still collecting pyrolysis products.

Process Use--

In September 1976, Dow Chemical was awarded a 4-year DOE contract (EX-76-C-01-2346), valued at $\$14\bar{M}$, to test the technical feasibility of recovering combustible gases by *in-situ* processing of Michigan Antrim oil shale [61]. The project site consists of 0.32 km^2 (80 acres) located in Fremont Township, Sunilac County, Michigan [62]. The three principal tasks of the program are:
1) the characterization and mapping of the Antrim shale resources,
2) the evaluation of three *in-situ* fracturing techniques, and
3) the demonstration of *in-situ* retorting [62].

---

[61] McNamara, P. H., C. A. Peil, and L. J. Washington. Characterization, Fracturing, and True *In-Situ* Retorting in the Antrim Shale of Michigan. In: Twelfth Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, Colorado, August 1979. pp. 353-365.

[62] Horst, B. I., and. E. I. Rosner. Laramie Energy Technology Center Process Evaluation (draft report). Contract No. 31-109-38-3764, U.S. Department of Energy, Laramie, Wyoming. May 25, 1979. 313 pp.

As of August 1979, experimentation with three fracturing methods -- hydraulic fracturing, chemical underream, and explosive underream -- was complete, and a time *in-situ* retorting trial had begun [61] (personal communication, C. A. Peil, Dow Chemical Company, to G. M. Rinaldi, Monsanto Research Corporation, August 15, 1979). Ignition conditions are considered to be critical for successful extraction. A sufficiently large mass of shale, with available fractures for needed air flow, must be sufficiently heated to produce sustained combustion. The ignition gas temperature will be controlled to about 530°C (990°F), and the heat input will continue for about 10 days [61].

Water Quality/Quantity Data--
No water flow diagram is available for the Dow experiments at this time. In addition, no process wastewater analysis are available; however, several experiments have been run on the DOE 10-ton experimental retort using Antrim shales. The analysis of these retort waters is presented in Tables A-13 and A-14.

TABLE A-13. 10-TON RETORT WATER ANALYSES ON ANTRIM SHALES[a] [32]

Parameter	Concentration, mg/L[a]	Parameter	Concentration, mg/L[a]
Calcium	7.6	TOC	1,975
Magnesium	31.9	COD	17,500
Sodium	22.2	TKN	4,880
Potassium	13	NH_3 as N	5,667
Carbonate	425	pH	8.4
Bicarbonate	11,225	Conductance	20,890
Sulfate	1,827	Hardness ($CaCO_3$)	286
Chloride	1,890	TDS	1,765
Nitrate	-	Total CO_3	6,100
Fluoride	14.8	Cadmium	<0.05
Boron	5.0	Selenium	0.96
Silica (SiO_2)	8	Mercury	0.05
Ammonium	6,200	Arsenic	<0.005

[a] Average of 5 values; data cited in Reference 14; however, original source of data was not given.

[b] Except pH, given in pH units.

TABLE A-14. TRACE ELEMENT COMPOSITION FOR MICHIGAN SHALE WASTEWATER [32, 63]
ppm

Element	Concentration	Element	Concentration
Uranium	-[a]	Bromine	0.520
Bismuth	0.001	Selenium	
Lead	0.120	Arsenic	0.011
Mercury	0.0002	Germanium	0.006
Tungsten	-[a]	Gallium	0.002
Tantalum	0.003	Zinc	6.900
Neodymium	-[a]	Copper	1.900
Praseodymium	-[a]	Nickel	0.005
Lanthanum	-[a]	Cobalt	0.051
Barium	0.012	Iron	1.100
Cesium	-[a]	Manganese	0.280
Iodine	0.200	Chromium	0.020
Antimony	0.026	Vanadium	0.011
Tin	0.005	Titanium	0.013
Molybdenum	0.049	Sulfur	69
Niobium	0.003	Phosphorus	39
Zirconium	0.003	Silicon	2.600
Strontium	0.020	Aluminum	0.075
Rubidium	0.013		

[a] Elements not reported, <0.001 ppm.

Geokinetics Process

Process Description--

The Geokinetics horizontal *in-situ* retorting process begins with the drilling of blast holes from the surface, through up to 46 m (150 ft) of overburden, and into the oil shale bed [64]. The

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[63] Martel, R. A. and A. E. Harak. Preliminary Results from Retorting Michigan Antrim Shale. LERC/TPR-77/1, LERC, ERDA, Laramie, Wyoming, July 1977.

[64] Lekas, M. A. Progress Report on the Geokinetics Horizontal *In-Situ* Retorting Process. In: Twelfth Oil Shale Symposium Proceedings, Colorado School of Mines, Golden, Colorado, August 1979. pp. 228-236.

holes are then loaded with explosives, which are fired to yield a rubblized mass of oil shale with increased permeability. During fragmentation, the surface undergoes noticeable uplift. A slope is created below the oil shale bed, allowing shale oil to drain to a sump for recovery by production wells, as shown in Figure A-21 [64].

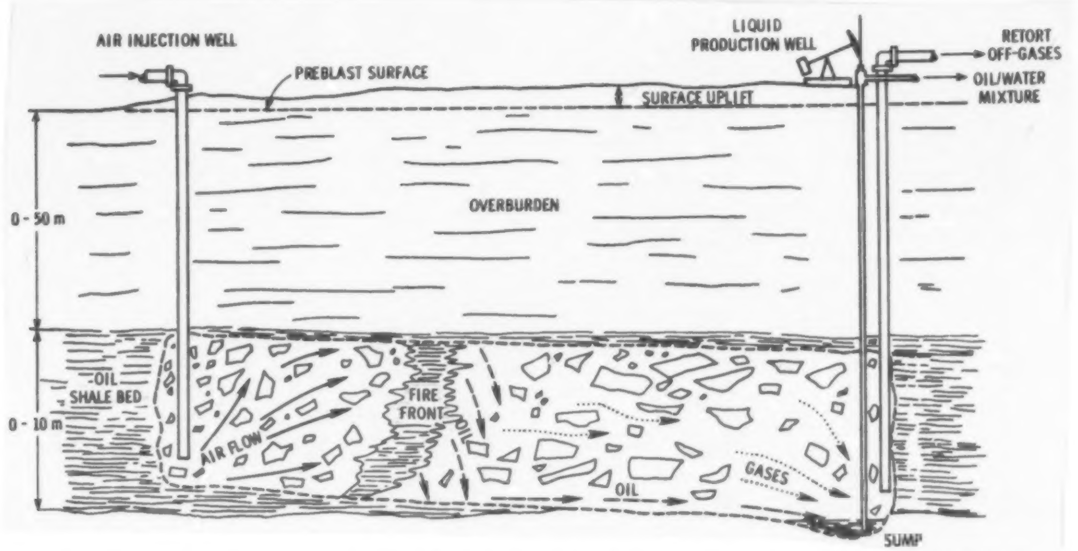
AIR INJECTION WELL
PREBLAST SURFACE
LIQUID PRODUCTION WELL
RETORT OFF-GASES
OIL/WATER MIXTURE
SURFACE UPLIFT
OVERBURDEN
0 - 50 m
OIL SHALE BED
0 - 10 m
FIRE FRONT
AIR FLOW
OIL
GASES
SUMP

Figure A-21. Sectional view of Geokinetics horizontal *in-situ* oil shale retort [64].

The oil shale is ignited with burning charcoal at the air injection wells, which are drilled at one end of the retort. Injected air establishes and maintains a horizontally moving burn front that occupies the entire cross section of the rubblized bed. Off-gases containing oil mist exit through output holes at the downstream end of the retort. Above ground, a mixture of water and shale oil is pumped by production wells to an oil-water separator tank. The aqueous layer is separated and sent to an evaporation pond, and the oil is pumped to product storage tanks. The entrained oil and water in the retort off-gases are removed by a demister; the recovered liquid is sent to the separator tank mentioned above.

Process Use--
On July 22, 1977, Geokinetics, Inc., signed a contract with the U.S. Energy Research and Development Administration (now the Department of Energy) to develop a process for explosive fragmentation and horizontal *in-situ* retorting of oil shale deposits that are located under shallow overburden [36]. Cooperative Agreement No. ET-76-A-03-1787, valued at about $9.2M̄, is intended to develop and improve the shale oil recovery technique studied by Geokinetics in laboratory and field work dating back to 1973

[36]. The project site, leased from the State of Utah in March 1975, is located in the northeast quadrant of Section 2, Township 14 South, Range 22 East, Uintah County [36, 64].

As of December 31, 1978, Geokinetics had blasted and burned 11 retorts at the "Kamp Kerogen" site, producing over 800 m^3 (5,000 bbl) of crude shale oil [64]. During July 1979, air emissions and water effluents from Geokinetics Retort No. 17 were sampled by MRC personnel under EPA contract 68-03-2550 to provide additional data for environmental characterization of *in-situ* oil shale retorting [65]. Geokinetics' future plans for research at Kamp Kerogen include: (1) burning a retort with a 9-m thick oil shale bed and blasting a full-sized retort (60 m wide, 60 m long, and 9 m thick) during 1979, (2) blasting a cluster of three full-sized retorts during 1980; and (3) burning the above cluster and blasting a second three-retort cluster during 1981, the burning of which will be completed in the first half of 1982 [64].

Water Quality/Quantity Data--
Presently, retort water is sent to an evaporation pond; longer term there are no known alternatives to this practice. Geokinetics wastewaters have been extensively characterized; available data is listed in Tables A-15 through A-18.

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[65] Delaney, J. L. Sampling and Analytical Plan for Environmental Characterization of *In-Situ* Oil Shale Retorting at Geokinetics, Inc., Kamp Kerogen, Retort 17. Contract No. 68-03-2550, U.S. Environmental Protection Agency, Cincinnati, Ohio. March 1979. 78 pp.

TABLE A-15. CHARACTERISTICS OF WASTEWATERS - GEOKINETICS mg/L

	Ground water[a] [66]	Retort water[b] [66]	Retort water[c] [67]	Evaporation pondwater[d] [67]
Alkalinity as $CaCO_3$	25,200	17,800	16,600	22,400
Hardness as $CaCO_3$	39	154	34	122
Bicarbonate	26,000	17,200	5,380	10,800
Carbonate	2,380	2,800	173	345
pH	9.33	8.56	8.9	8.9
Conductivity (μmhos/cm)	36,300	34,000	11,200	20,000
BOD			2,000	
COD	6,090	3,700	7,200	10,900
TIC			1,100	2,200
TOC			2,150	2,900
Chloride	2,200	3,000	1,100	3,300
Cyanide	0.11	13.3	95	266
Phenols	0.19	11.6	37.8	24
Oil and grease	3.33	103	186	648
Surfactants as MDAS	4.31	23.2		
Fluoride	93.3	35.2	15.6	42
Total phosphate	5.02	2.1	4.30	1.77
Ortho phosphate	2.17	1.07	1.30	1.77
TS			10,200	29,100
TDS	37,600	22,100	9,400	28,400
TVS			1,900	4,300
TDVS			2,100	4,000
Ammonia as N	25	1,270	870	1,200
Ammonium as N			317	437
Nitrate as N	6.21	34.2	9,500	20,000
Nitrite as N	0.39	1.33	0.08	0.07
TKN			1,230	1,250
Organic N			355	50
Total sulfur			1,230	4,200
Sulfate	11,100	609	825	3,080
Sulfide	17	447	0.2	1.14
Sulfite			400	1,100
Tetrathionate			1,080	3,700
Thiocyanate			325	1,030
Thiosulfate			<25	<25
Gross alpha (pCI/L)	6.18	8.29		
Gross beta (pCI/L)	17.8	26.5		

[a] Average of 8 values.

[b] Average of 11 values; 1 from retort #15, 5 from retort #14, 5 from retort #16.

[c] Single value from retort #17.

[d] Single value.

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[66] Hutchinson, D. L. Appendix D, GKI Water Quality Study. Progress Report.

[67] Preliminary data generated by Monsanto Research Corporation for the U.S. Environmental Protection Agency under contract 68-03-2550.

TABLE A-16. TRACE METALS IN GEOKINETICS' WASTEWATERS mg/L

	Ground water[a] [66]	Retort water[b] [66]	Retort water[c] [67]	Evaporation pond water[d] [67]
Aluminum as Al			0.35	0.51
Antimony as Sb	0.24	0.011	0.11	0.44
Arsenic as As	0.46	2.55	1.6	15
Barium as Ba	0.71	0.54	0.22	0.37
Beryllium as Be	0.009	0.009	<0.00004	<0.00004
Bismuth as Bi	0.30	0.059		
Bromide as Br	0.152	0.18		
Boron as B	87.85	60.55	61	186
Cadmium as Cd	0.14	0.084	0.02	0.02
Calcium as Ca	7.11	32.58	6.6	11
Chromium as Cr	0.10	0.078	0.04	0.06
Cobalt as Co	0.28	0.56	0.11	0.25
Copper as Cu	0.20	0.209	0.04	0.07
Germanium as Ge	0.009	0.044		
Iron as Fe	13.18	13.99	0.80	9.6
Lead as Pb	0.17	0.642	0.14	0.20
Lithium as Li	0.24	0.179		
Magnesium as Mg	12.79	17.49	8.9	31
Manganese as Mn	0.383	0.937	0.01	0.03
Mercury as Hg	0.0007	0.004	0.04	0.03
Molybdenum as Mo	0.41	11.91	0.27	6.9
Nickel as Ni	0.43	1.62	0.49	0.76
Potassium as K	53.80	121.43	29	57
Selenium as Se	0.97	0.215	0.02	0.28
Silicon as Si	13.3	8.4	0.31	0.96
Silver as Ag	0.041	0.135	0.05	0.13
Sodium as Na	10,455.38	9,392	2,800	8,300
Strontium as Sr	0.035	0.002	0.69	0.89
Thallium as Tl			<0.05	<0.05
Tin as Sn		0.168	0.05	0.1
Titanium as Ti			0.02	0.04
Vanadium as V	0.31	0.43	0.12	0.3
Zinc as Zn	0.15	0.095	0.06	0.1

[a] Average of 8 values.

[b] Average of 11 values; 1 from retort #15, 5 from retort #14, 5 from retort #16.

[c] Single value from retort #17.

[d] Single value.

TABLE A-17. ORGANIC PRIORITY POLLUTANTS IN GEOKINETICS WASTEWATERS [67][a] (μg/L)

	Retort water	Evaporation pond water	Method blank
Fluorene	-	-	0.4
Acenaphthylene	11	92	-
Bis(2-ethylhexyl) phthalate	0.5	3.8	9.0
Anthracene/phenanthrene	3.6	10	1.3
Diethyl phthalate	-	3.5	13
Di-n-butyl phthalate	-	0.8	0.6
Dimethyl phthalate	-	-	1.8
Butyl benzyl phthalate	-	-	0.5
Di-n-octyl phthalate	-	1.5	0.6
Phenol	670	230	-
Methylene chloride	11	22	0.8
Trichloroethylene	1.7	2.8	1.4
Benzene	370	67	0.5
Tetrachloroethylene	0.9	0.5	-
Toluene	280	64	3.6
Ethylbenzene	45	29	0.2
Chloroform	-	2.0	-
Acrolein	-	360	-
Acrylonitrile	250	1,700	-
Fluoranthene	-	8.3	-
Pyrene	-	3.2	-
Chrysene	-	0.9	-
Nonpriority pollutants observed			
Acetone	~4,000	~900	~50
Xylenes	~250	~68	~0.5
n-Propyl benzene	~120	~49	
Trimethyl benzene		~400	

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[a] Wastewaters were analyzed for all of EPA's organic priority pollutants, however, only those compounds which were found above detection limits are listed. Detection limits for all organic priority pollutants are listed in Table A-18.

TABLE A-18. DETECTION LIMITS[a] FOR ORGANIC PRIORITY POLLUTANTS

Compound	Concentration, μg/liter
Acids:	
2-Chlorophenol	0.09
Phenol	0.07
2,4-Dichlorophenol	0.1
2-Nitrophenol	0.4
p-Chloro-*m*-cresol	0.1
2,4,6-Trichlorophenol	0.2
2,4-Dimethylphenol	0.1
2,4-Dinitrophenol	2.0
4,6-Dinitro-*o*-cresol	40.0
4-Nitrophenol	0.9
Pentachlorophenol	0.4
Volatiles:	
Chloromethane	5.0
Dichlorodifluoromethane	2.0
Bromomethane	5.0
Vinyl chloride	5.0
Chloroethane	5.0
Methylene chloride	0.1
Trichlorofluoromethane	0.3
1,1-Dichloroethylene	0.5
1,1-Dichloroethane	0.4
Trans-1,2-dichloroethylene	0.7
Chloroform	0.3
1,2-Dichloroethane	2.0
1,1,1-Trichloroethane	0.3
Carbon tetrachloride	0.4
Bromodichloromethane	0.3
Bis(chloromethyl) ether	5.0
1,2-Dichloropropane	0.8
Trans-1,3-dichloropropane	0.7
Trichloroethylene	0.2
Dibromochloromethane	0.4
Cis-1,3-dichloropropene	1.5
1,1,2-Trichloroethane	0.5
Benzene	0.2
2-Chloroethyl vinyl ether	5.0
Bromoform	1.0
Tetrachloroethylene	0.2
1,1,2,2-Tetrachloroethane	0.3
Toluene	0.1
Chlorobenzene	0.2
Ethylbenzene	0.1
Direct injectables:	
Acrolein	200
Acrylonitrile	100
Base/neutrals:	
1,3-Dichlorobenzene	0.02
1,4-Dichlorobenzene	0.04
Hexachloroethane	0.1
1,2-Dichlorobenzene	0.05
Bis(2-chloroisopropyl) ether	0.06
Hexachlorobutadiene	0.08
1,2,4-Trichlorobenzene	0.09
Naphthalene	0.007
Bis(2-chloroethyl) ether	0.07
Hexachlorocyclopentadiene	0.2
Nitrobenzene	0.08
Bis(2-chloroethoxy) methane	0.06
2-Chloronaphthalene	0.02
Acenaphthylene	0.02
Acenaphthene	0.04
Isophorone	0.06
Fluorene	0.02
2,6-Dinitrotoluene	0.2
1,2-Diphenylhydrazine	0.02
2,4-Dinitrotoluene	0.02
N-nitrosodiphenylamine	0.07
Hexachlorobenzene	0.05
4-Bromophenyl phenyl ether	0.1
Phenanthrene	0.01
Anthracene	0.01
Dimethyl phthalate	0.03
Diethyl phthalate	0.03
Fluoranthene	0.02
Pyrene	0.01
Di-n-butyl phthalate	0.02
Benzidine	0.02
Butyl benzyl phthalate	0.03
Chrysene	0.02
Bis(2-ethylhexyl) phthalate	0.04
Benz(a)anthracene	0.02
Benzo(b)fluoranthene	0.02
Benzo(k)fluoranthene	0.02
Benzo(a)pyrene	0.02
Indeno(1,2,3-cd)pyrene	0.02
Dibenzo(a,h)anthracene	0.02
Benzo(g,h,i)perylene	0.01
N-nitrosodimethylamine	0.8
N-nitrosodi-n-propylamine	0.2
4-Chlorophenyl phenyl ether	0.03
3,3'-Dichlorobenzidine	1.0
Di-n-octyl phthalate	0.9

[a] Based on the lowest quantifiable area obtained from gas chromatography/mass spectrometry.